STUDIES ON IONIC POLYMERISATION

by

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TO MY FAMILY

ACKNOWLEDGEMENTS

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ABSTRACT

The reaction between anionic polystyrene and cationic polyTHF has been examined and shown to result virtually quantitatively in coupling of the two polymers. The reaction has been exploited to prepare AB, ABA and $(AB)_n$ block copolymers and g.p.c. analysis has shown these materials to be free from contamination by homopolymer.

The reaction between anionic poly(α-methylstyrene) and living polyTHF has also been examined. The efficiency of the coupling reaction was shown to be about 20%, and this efficiency was relatively insensitive to the temperature of the reaction. The competing reaction was identified as one of β-proton transfer resulting in a hydrogen-terminated poly(α-methylstyrene) chain and a polyTHF molecule possessing terminal unsaturation. Transformation of the living poly(α-methylstyrene) into a polymeric Grignard reagent before reaction seemed to have no significant effect on the efficiency of the linking process.

No linking was observed on reaction of living polyTHF and 1,1-diphenylethylene anions.

Reaction of pyridine with living polyTHF was found to be quantitative. Possible synthetic and analytical developments arising from this and similar reactions are discussed.

Six four-membered cyclic sulphones were prepared and tested for polymerisation with anionic, cationic and free-radical initiators. No polymerisation was observed.

Sulpholan was incorporated into an alternating copolymer by (a) generating the αα'dianion on reaction with butyl lithium, and (b) subsequently reacting the dicarbanion with various dihalides

such as thionyl chloride and hexamethylene dibromide. The co-polymers were found to be thermally unstable at temperatures above 420K.

Low molecular weight diadducts (the 2,5-diacetyl-sulpholan and 2,5-dimethane-sulphonyl sulpholan) were prepared for biological testing.

A cationic to anionic transformation which involved reaction of cinnamyl terminated polyTHF (I) with BuLi was studied with model compound analogues of I to ascertain if the desired product was produced quantitatively. It was found that a mixture of products was obtained when the reaction was carried out in THF.

A kinetic study of the polymerisation of acenaphthylene in nitrobenzene with propionyl and nitronium hexafluoroantimonate initiators was discovered to be first order with respect to monomer concentration and the same k_p was recorded for both catalyst systems. A β-proton transfer reaction from the growing end was found to be operating.

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PART A

BLOCK COPOLYMERS

CHAPTER 1

INTRODUCTION

1.1. Underlying Ideas

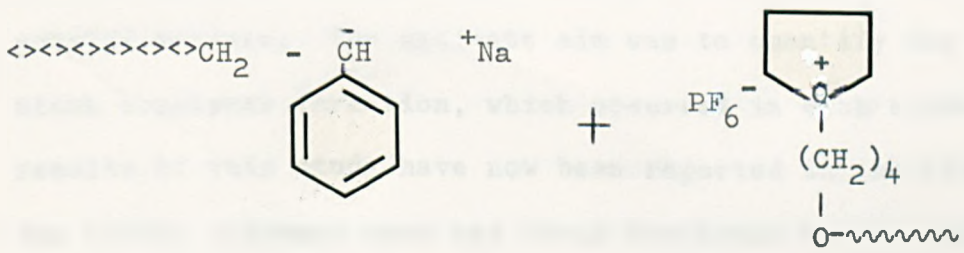
Block copolymers are becoming increasingly important for technological applications, finding uses as elastomers, adhesives, thermoplastics etc.

The development of the "living" anionic polymerisation system by Szwarc and co-workers[1] enabled block copolymers of the type $(AB)_n$ to be prepared from monomers susceptible to addition polymerisation, and allowed these polymers to become commercially significant. For example, the synthesis of a styrene - butadiene block copolymer with an ABA structure formed from the consecutive anionic polymerisation of the component monomers led to the introduction of an important industrial thermoplastic elastomeric material[2].

The success of this technique is, however, dependent on the stabilities of the anions generated. In the example given, the polystyryl carbanion can initiate the polymerisation of butadiene and vice versa, but such systems are rare. For many monomer combinations, the second monomer is initiated by the polymeric anion of the first, but the resultant anion is too stable to activate the polymerisation of a fresh portion of the first component. Consider mono- or di-functional living polystyrene which initiates the polymerisation of ethylene oxide; the alkoxide ion thus produced is too weak a nucleophile to initiate in turn the polymerisation of styrene[3]. When restricted to monomers whose anions can initiate one another, the anionic method has proved to be one of the most efficient in producing a mono-disperse $(AB)_n$ block copolymer of well defined structure. The most industrially important monomers that undergo this type of polymerisation process are styrene, α-methylstyrene, isoprene and butadiene.

In principle, "living" cationic polymerisation systems may also be devised to prepare polymers with terminal cations, either monofunctional or difunctional. However, in practice, because of the ease of proton transfer in cationic polymerisations, and the great reactivity of organic cations comparatively few monomers form sufficiently stable cations, and of these tetrahydrofuran (THF) is by far the best known and most studied.[4,5]

If "living" polymeric anion and cation solutions are combined and if an addition reaction between the two species occurs, block copolymers may be formed. This is illustrated with polystyrene and polyTHF in equation (1.1).



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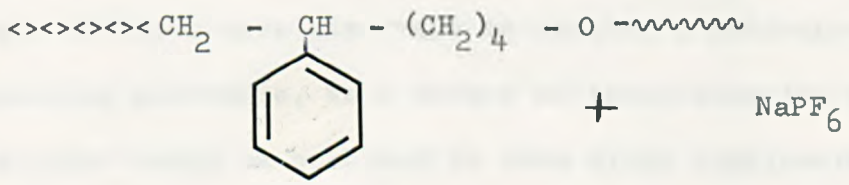


Such a process may in theory be extended to form AB, ABA, BAB and $(AB)_n$ block copolymers by choosing the appropriate functionalities of the component homopolymers.

This synthetic route has been reported previously for the reaction between living polyTHF and living polystyrene but only as a brief communication[6]. Infra-red spectroscopy was used to identify the styryl and tetramethylene oxide units present

in a material precipitated from methanol. As homopolyTHF is soluble in this solvent, block copolymer had been undoubtedly formed, but the efficiency of the coupling process was not examined. The techniques used for the preparation of "living" polymeric anions have remained largely unaltered for twenty years, whereas significant developments have occurred in the synthesis of "living" polyTHF in the last ten years. Vofsi's method[6] has been superseded by that of later workers[7], and their method was easily adapted to produce mono- and di-functional "living" polyTHF of low polydispersity.

In this thesis a study is reported on the linking efficiency of various "living" anions, in particular those of polystyrene and of the α-methylstyrene tetramer with mono- and/or di-functional polyTHF cations. The ultimate aim was to quantify the amount of block copolymer formation, which occurred in each system and the results of this study have now been reported in the literature[8,9]. The living polymers used and their syntheses are described in detail in the Experimental Section.

In parallel with this approach to the synthesis of new block copolymers attempts were also made to develop a cationic-to-anionic transformation procedure, as a method of increasing the number of monomers which could be combined to form block copolymers. This formed part of a general study of transformation reactions, some of which, anionic-to-cationic[10] and anionic-to-free radical[11] have already been reported. In addition, work was started on the use of tertiary aromatic amines as terminating or linking agents for polymers. This work also had the ultimate goal of preparing new block copolymers, although only an initial feasibility study is reported in this thesis.

The underlying chemistry of these separate avenues of research will be covered in greater depth later in this section, but to comprehend fully the scope and limitations of the techniques to be described, it is first necessary to be aware of the characteristics of the two mechanisms of addition polymerisation used in the work, the anionic and cationic processes. They are reviewed briefly in two distinct sections and, where applicable, special emphasis is laid on those points relevant to block copolymer synthesis.

1.2. Anionic Polymerisation

It was about 1911, that the technique of anionic polymerisation first attained commercial significance, when patents on the use of alkali metals as initiators for isoprene polymerisation were issued to Harries[12] in Germany and Matthews and Strange[13] in the United Kingdom. At the time the propagation mechanism was unknown; nevertheless, extensive use of the process was made, especially in Germany during World War One , for the production of a synthetic rubber based on 2,3-dimethyl butadiene.

Schlenk and his co-workers[14] pioneered the study into the reaction between alkali metals and unsaturated organic compounds, using sodium and phenyl substituted ethylenes such as stilbene and 1,1-diphenylethylene. They showed that di-sodium adducts were formed by stilbene and di-sodium dimers with 1,1-diphenylethylene. When styrene was used, a polymer was formed.

1.2.1. Initiators

In 1928 Schlenk[15] demonstrated that alkali metals could react with polycyclic hydrocarbons in polar solvents, such as ethers, to yield highly coloured adducts. The products of the reaction involving

sodium and naphthalene or biphenyl were shown to be capable of initiating polymerisation of styrene or butadiene[16].

Ziegler et al.[17-20] were the first to consider the use of alkyl lithiums as initiators, and reported on the mechanism occurring in the polymerisation of dienes. Ziegler[21] proposed the classic scheme for polymerisation by alkali metal alkyls which is shown in equation (1.2), with butyl lithium as a typical initiator.

$$Bu^{-}Li^{+} + CH_2{=}CH{-}CH{=}CH_2 \longrightarrow Bu{-}CH_2{-}CH{=}CH{-}CH_2^{-}Li^{+} \qquad (a)$$

$$n(CH_2{=}CH{-}CH{=}CH_2) + Bu{-}CH_2{-}CH{=}CH{-}CH_2^{-}Li^{+} \qquad (1.2)$$

$$\downarrow \qquad (b)$$

$$Bu(CH_2{-}CH{=}CH{-}CH_2)_{\overline{n}}CH_2{-}CH{=}CH{-}CH_2^{-}Li^{+}$$

Ziegler proposed that there are two distinct processes operating, the initiation stage (a) and the propagation stage (b).

When direct initiation by alkali metal was carried out, the mechanism proceeded via the di-adduct which could propagate at both ends: equation (1.3):

$$\text{Initiation} \quad CH_2{=}\overset{CH_3}{\overset{|}{C}}{-}CH{=}CH_2 + Na \longrightarrow Na^{+}\,{}^{-}CH_2{-}\overset{CH_3}{\overset{|}{C}} = CH{-}\dot{C}H_2$$

$$\text{Propagation} \quad 2\,Na^{+}\,{}^{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}\dot{C}H_2 \rightarrow Na^{+}\,{}^{-}CH_2{-}\overset{CH_3}{\overset{|}{C}}{=}CH{-}CH_2{-}CH_2{-}CH{=}\overset{CH_3}{\overset{|}{C}}{-}CH_2^{-}Na^{+} \qquad (1.3)$$

Therefore, the existence of mono- and di-functional polymeric chains was recognized quite early, as was the concept of a terminationless polymerisation process.

(1.7) $$T_c = \Delta H/R[\ln(A_p/A_d) + \ln m]$$

where T_c = Ceiling temperature

ΔH = Enthalpy of polymerisation

R = Gas constant

A_p = Pre-exponential factor for propagation

A_d = Pre-exponential factor for depropagation

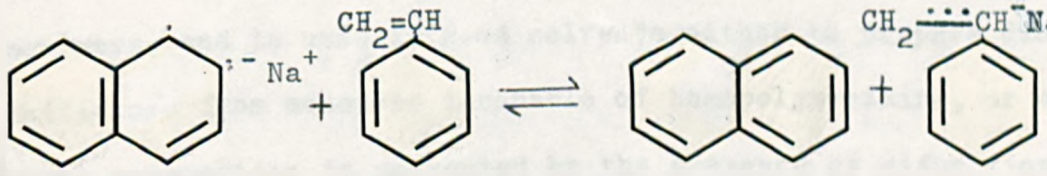
m = monomer concentration

1.2.2. Difunctional initiation

Szwarc and his co-workers in the late 1950's quantified the ideas of Ziegler and developed conditions which enabled "living" systems to be generated reproducibly[22]. They showed that if sodium naphthalene in THF were used as an initiator for vinyl and diene polymerisations, the mechanism of initiation was one of electron transfer and with sufficiently pure systems termination could be avoided. Successive additions of monomers were found to cause the polymer chains to grow until all the monomer was consumed. The initiator is formed by the transfer from sodium metal of an electron to the lowest unoccupied π-orbital of the naphthalene, to generate the sodium naphthalene adduct (equation (1.4.)). The equilibrium is well over on the right-hand-side in good cation solvating solvents such as THF, but can be displaced to yield sodium dust and naphthalene by replacing such a solvent with an inert hydrocarbon like heptane or benzene.

(1.4.)

Sodium naphthalene initiates in turn by electron transfer to monomer to form the monomer radical anion (I), which dimerises to produce a dimer dianion (II), capable of polymerising further monomer at each end. The process is illustrated with sodium naphthalene and styrene in equations (1.5.) and (1.6.).



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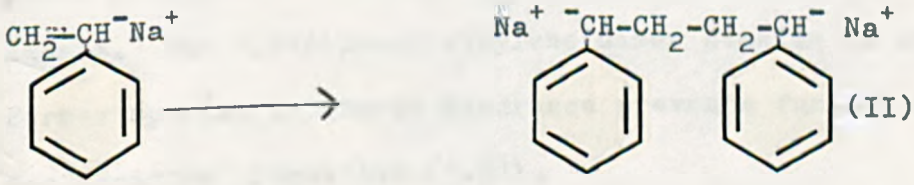


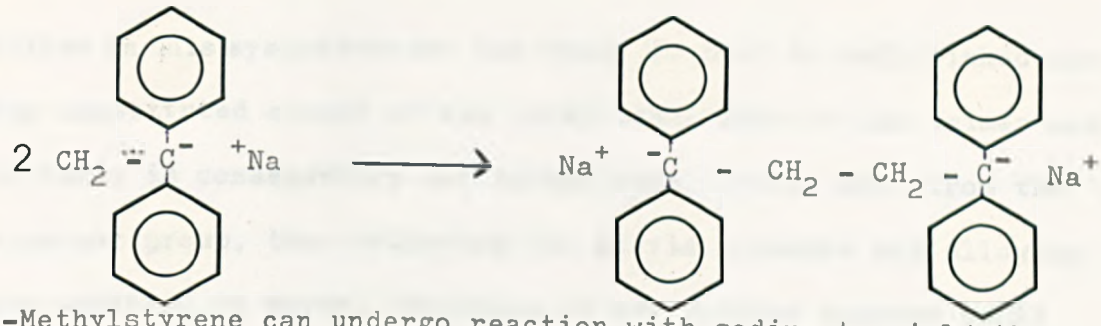
(1.6.)

The generation of the monomer radical anion and its dimerisation rapidly removes the sodium naphthalene, as indicated by the rapid transformation of the green colour of the initiator solution into the bright red which is characteristic of the benzyl anion. The dimerisation stage (equation (1.6)) involves tail to tail bonding which results in a structure that gives maximum resonance stabilisation to the terminal carbanions. The dimers can then propagate by conventional head to tail linking, and this allows perpetuation of the benzylic anion. The propagation (equation (1.2)) is reversible but many monomers have equilibrium concentrations which are extremely low and so propagation may be regarded as going to completion. However, α-methylstyrene, principally because of steric factors, has a high equilibrium monomer concentration $[M]_e$ (0.7M* at 293K[24]) at ambient temperatures, (equation (1.7.)).

1.2.3. Alkali metal initiation

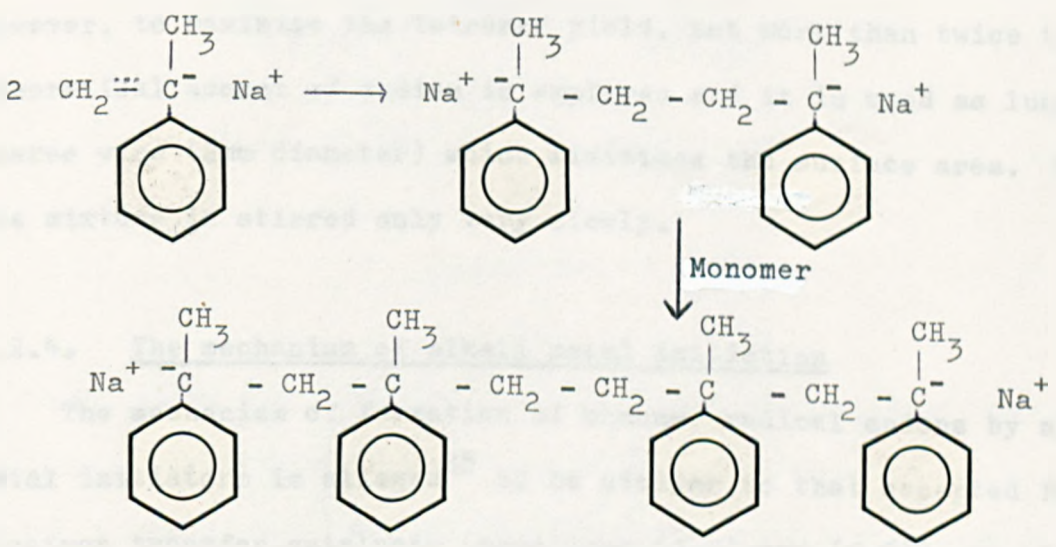
The direct reaction of monomer with alkali metal, being heterogeneous, is controlled by the surface area of the metal. Even when this is maximized by preparing the metal as a dispersion or a mirror, initiation relative to propagation is generally slow, and materials of unpredictable molecular weights with broad distributions result. This direct method is consequently not favoured for producing polymers, and is used in good solvents either to prepare dianionic initiators from monomers incapable of homopolymerising, or copolymers where propagation is prevented by the presence of difunctional linking agents. The 1,1-diphenylethylene dimer dianion is an example of the former species as steric hindrance prevents further head to tail monomer addition (equation (1.8)).

* This value depends on the solvent employed for the polymerisation.



(1.8)

α-Methylstyrene can undergo reaction with sodium to yield the tetramer specifically at monomer concentrations below that existing in equilibrium with living poly (α-methylstyrene) at the experimental temperatures. The mechanism involved for tetramer formation is as follows. The initial step involves the formation of radical anions by direct reaction of monomer with sodium metal and their subsequent dimerisation by tail to tail linking to form dimer dianions, possessing resonance stabilised benzylic anions (equation (1.9)).



(1.9)

Addition of a monomer unit to each end of the dimer dianion would formally constitute the first stage of a propagation step to form polymer, but with monomer concentrations below that in equilibrium with poly (α-methylstyrene) anions, propagation is not allowed thermodynamically. However, it is observed that tetramer is formed under these conditions, but no higher oligomers. Therefore, the reason put forward for its formation is that the thermodynamics

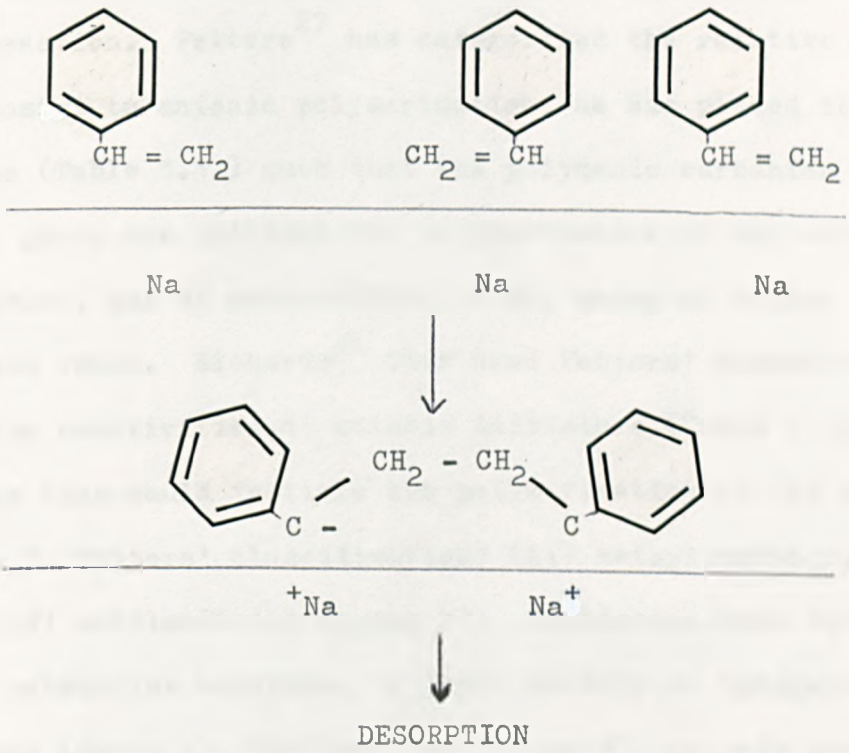
differ in this system because the dimer is tail to tail linked and the substituted carbon of the penultimate unit of the trimer and tetramer is consequently one carbon atom further away from the terminal group, thus relieving the steric pressure and allowing the addition to occur. Addition of any further monomer would result in the creation of head to tail linked units; the steric restrictions would be restored and hence the higher oligomers would be unstable.

The rate of reaction of α-methylstyrene with sodium is mainly dependent on the surface area of the sodium and the rate of stirring. (see Section 2.3.4.). If a large surface area of sodium is used and rapid stirring, the prime reaction of monomer with metal is enhanced, and dimer and trimer as well as tetramer are formed. However, to maximize the tetramer yield, not more than twice the theoretical amount of sodium is employed and it is used as lumps or coarse wire (2mm diameter) which minimizes the surface area. Further, the mixture is stirred only very slowly.

1.2.4. The mechanism of alkali metal initiation

The mechanism of formation of monomer radical anions by alkali metal initiators is alleged[25] to be similar to that accepted for the electron transfer catalysts (equations (1.5) and (1.6)), as it likewise involves the initial electron transfer from the metal to the monomer which leads to the formation of a radical anion. However, Richards[26] has recently questioned the formation of radical anions as intermediates in the reaction of monomers with alkali metals. He suggests that the adsorptive power of the monomer plays a prominent role in the process; the monomer is adsorbed strongly onto the metal surface where it has sufficient rotational ability to interact with

the metal and reacts subsequently with another adsorbed monomer unit to form an adsorbed dimer dianion, the desorption of which is aided by the solvating power of the solvent (THF). Thus, the dimer dianion enters the solution without intermediate formation of the radical anion (equation (1.10)).



(1.10)

Richards cites two examples to support this mechanistic view:
(a) The Wurtz reaction between saturated alkyl halides and an alkali metal which is very vigorous in THF, is immediately subdued by introducing monomer into the system, and the products obtained under specific stoichiometric conditions are alkyl terminated dimers. This shows that an easily polarisable monomer is adsorbed preferentially onto the metal surface (the alkyl halide molecules possessing only σ bonds are not readily polarisable) and the dimer dianion is formed.
(b) Alkyl tosylates (p-toluene sulphonates) react as efficiently as alkyl bromides with "living" polymer in a homogeneous system to form

the adduct virtually exclusively. However, in contrast to the alkyl bromides on reaction with monomer and alkali metal in THF they give only low yields of oligomeric adducts. This difference in behaviour is attributed to the polarisability of the tosylate ligand. It is able to compete effectively with the monomer for adsorption sites on the alkali metal and this permits coupling to occur as a major side reaction. Fetters[27] has categorised the relative reactivities of monomers to anionic polymerisation; he has placed them in five classes (Table 1.1.) such that the polymeric carbanion of a monomer in one group can initiate the polymerisation of any other member of that group, and of every member of any group of higher number, but not vice versa. Richards[26] then used Fetters' classification to rank the reactivities of anionic initiators (Table 1.2) by considering whether they could initiate the polymerisation of (i) styrene, (group 1, Fetters' classification) (ii) methyl methacrylate (group 2) and (iii) acrylonitrile (group 4). Initiators were divided into three categories according to their ability to initiate all three monomers (group A), the last two (group B), or only acrylonitrile (group C).

Both these schemes are meant to indicate the order of reactivity which exists without the use of strongly co-ordinating additives such as crown ethers or cryptates.

TABLE 1.1.

RELATIVE REACTIVITIES OF MONOMERS.[27]

Group	Monomers
1	Styrene, α-methylstyrene, butadiene, isoprene, o- and p-halostyrene,* 2- and 4-vinyl pyridine, 1,2-dihydronaphthalene, triethyl vinyl germanium, triethyl vinyl tin.
2	Acrylates, methacrylates
3	Ethylene oxide, ethylene sulphide, propylene sulphide, dimethyl ketone, formaldehyde.
4	Acrylonitrile, methacrylonitrile, mono- and di-isocyanates, carbodiimides, N-substituted maleimides.
5	Nitroethylene, nitropropene, Cyanogen, vinylidene cyanide.

* It has been reported subsequently that the p-bromostyrene anion does not polymerise styrene.[28]

TABLE 1.2.

RELATIVE REACTIVITIES OF ALKALI METAL INITIATORS.[26]

Group	Initiators
A	Metal, organometallic compounds, Mono- and dimetal adducts of aromatic hydrocarbons, Dimetal adducts of aromatic carbonyl compounds, azomethines and nitriles
B	Monometal adducts of aromatic carbonyl compounds, azomethines and nitriles Dimetal adducts of aromatic azo, azoxy and nitroso compounds
C	Monometal adducts of aromatic azo, azoxy and nitroso compounds Metal alkoxides

1.2.3. Solvents

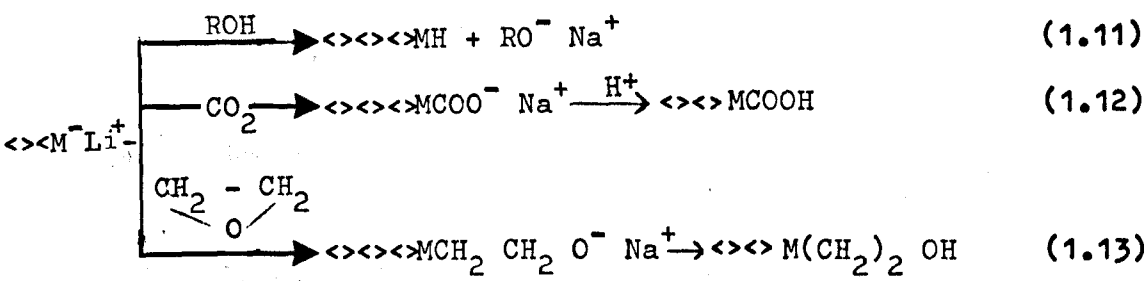
The successful use of the anionic polymerisation technique to prepare high polymers requires pure reagents and solvents, and stringent experimental conditions. The solvents can be divided into two categories, those that are inert, for example hexane, cyclohexane, etc.; and those which are good cation solvators, such as THF, the glymes and hexamethyl phosphoramide. The degree of solvation of the active ends in inert solvents is very small, thus the rate of propagation is lower than in good solvents. Moreover, electron transfer catalysts cannot be prepared or used in inert solvents, as a contribution from the free energy of solvation of the alkali metal is required. Evidence for this is that replacing THF by benzene in the preparation of sodium naphthalene results in the formation of naphthalene and sodium sand.

Therefore, only "addition initiators" such as the lithium alkyls can be used in inert solvents and because alkyl dilithium compounds are very difficult to prepare pure and are generally insoluble in hydrocarbons such solvents are usually employed for the preparation of mono-functional living polymers. By contrast, in good cation solvating solvents both electron transfer and alkyl lithium initiators can be used and mono- and di-functional polymers can be made by rapid propagation. When butadiene is polymerised in a hydrocarbon with an alkyl lithium initiator, the product contains 35% cis-1,4, 52% trans-1,4 and only 13% vinyl (1,2)[29]. In contrast, the polybutadiene formed by initiation with sodium naphthalene in THF contains 0% cis-1,4, 9% trans-1,4 and 91% vinyl[30]; the presence of even small quantities of THF in the hydrocarbon solvent increases dramatically the vinyl content[31].

For optimum elastomeric properties it was thought that a high cis-1,4 content should be prepared. However, it was found experimentally that the only important requirement was that the material possessed a low vinyl content. This is because a cis to trans isomerisation occurs during the vulcanisation stage[32], hence the polymer obtained by polymerisation in an inert solvent gives the superior product.

1.2.6. Termination

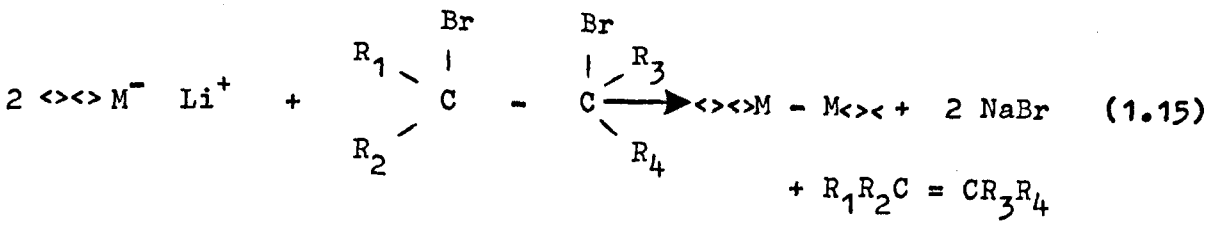
Because living polymers are able to retain their activity at the chain ends, termination reactions may be introduced by the experimenter to produce polymers with desired terminal functional groups. The polymers may be mono- or di-functional depending on the nature of the initiator; if di-functional terminating reagents are used, then polymer chains can link together. Typical reagents employed for this purpose include proton donors such as water, methanol etc., carbon dioxide[33], ethylene oxide[3] and dihalides[34]. The resulting terminal groups generated are given in Equations (1.11) to (1.14).



$$2\langle\rangle\langle\rangle\langle M^{-}\ Li^{+} + RBr_2 \longrightarrow \langle\rangle\langle\rangle\langle\rangle\ M - R - M\ \langle\rangle\langle\rangle + 2Li\ Br \qquad (1.14)$$

For the process depicted in equation (1.14) the dihalide should be added slowly in a controlled manner until the end-point is reached, in order to maximize the coupling process. The predominance of metathetical linking reactions such as equation (1.14) depends on

the nature of the alkyl ligand; vicinal dihalides react by elimination to produce a head to head linked homopolymer and the corresponding olefin[34] (equation (1.15)).



(1.15)

1.2.7. Summary

Anionic polymerisation is a convenient way of preparing polymers of a number of common vinyl or diene monomers with predetermined molecular weights of narrow distributions. The absence of an innate termination step allows the introduction of a functional group at one or both ends of the polymer chain. The most recent review on the subject is by Richards[26].

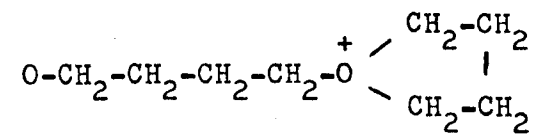
1.3. Cationic Polymerisation

Probably the earliest quantitative experiments on what are now known as cationic polymerisations were made by Williams[35] with styrene and stannic chloride, and by the early 1940's the general belief had become established that in reactions initiated by metal halides the active species is a cation.

Since then work by Evans, Plesch, Pepper, Kennedy, Ledwith and others has opened up the subject as a new area of polymer science. The kinetic and mechanistic aspects of cationic polymerisations have been reviewed comprehensively up to 1963 by Plesch[36]. In a later publication[37] he has concluded that many so-called cationic polymerisations do not proceed through ionic, but through covalently bonded, intermediates; these are referred to as "pseudo-cationic polymerisations". For the purpose of this section a very brief outline of the basic chemistry involved in the polymerisation by an oxonium ion mechanism is given. The specific aspects of direct relevance to the present study are explained in greater detail.

1.3.1. Monomers

Cyclic oxygen compounds may be polymerised cationically and these include cyclic ethers, formals and lactones. The polymerisation of THF has been investigated quite extensively[4,5]. Meerwein[38] was first to show that polymerisation could be induced by a wide range of cationic initiators. It is now accepted that the propagating species is a tertiary oxonium ion[39] (A).

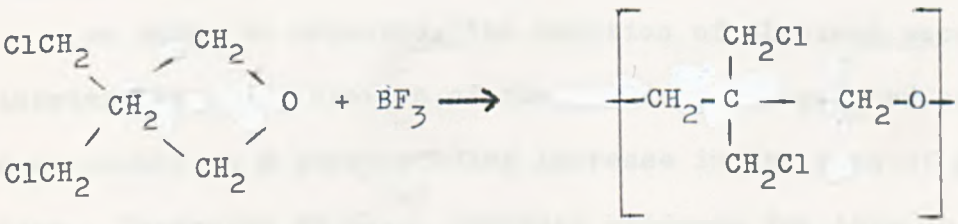


(A)

Thus cationic polymerisation has displayed properties under controlled conditions peculiar to a living polymer. Berger et al.[6] have demonstrated how poly(styrene-b-THF) block copolymers are formed by reaction of the living polymers. However, their work was only exploratory and left many questions unanswered; a more detailed discussion of this point is given in section 3.2.1.

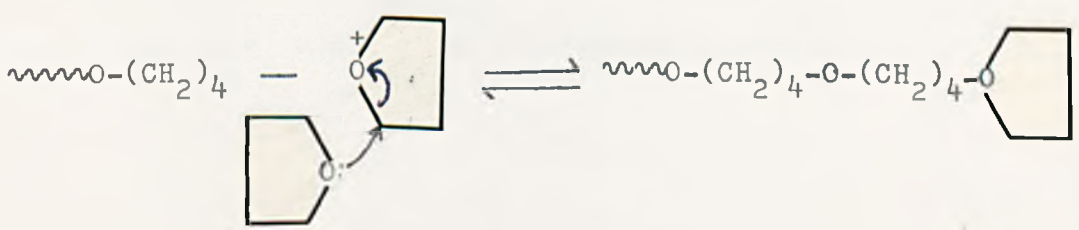
1.3.2. Initiators

The most commonly used initiators are metal halides. It is known that these, alone, do initiate polymerisation of cyclic oxygen compounds.An example of cyclic ether which was used commercially is'Penton' . The polymerisation (by ring opening analagous to THF) was carried out in the range 153K to 298K with BF_3 or $BF_3.Et_2O$ as the initiator[40](equation (1.16.)).



(1.16)

Other initiators which cause a ring-opening polymerisation of THF include strong acids (CF_3CO_2H) and salt initiators (p-chlorophenyl-diazonium hexafluorophosphate)[5]. It is well established[41] that using PF_6^- as the counter-ion (X^-) in polar and aromatic solvents and in bulk enables high molecular weight polyTHF to be obtained and a living system without termination can be observed . The propagation stage is considered to proceed in equilibrium (equation (1.17)).



(1.17)

Reactions such as that shown in equation (1.17) are the subject of a number of original and review papers[42-45].

1.3.3. Solvents

For preparative cationic polymerisation work great care is required in the choice of solvent. The dielectric constant (ε) is a poor guide to the solvating power of the solvent; for example, benzene gives higher rates and D.P.'s than would be expected from its ε[46].

Some common solvents employed for cationic polymerisation are chlorinated hydrocarbons such as dichloromethane (medium ε), nitrobenzene (high ε) and less frequently carbon disulphide (low ε). For the work reported in this thesis THF was polymerised in bulk; these systems are more rare.

As might be expected, the addition of electron acceptors to increase the dissociation of the terminal ion-pair by complexation does result in a corresponding increase in the rate of polymerisation. Panayotov et al.[47] provided evidence for this in a study of the polymerisation of styrene by BF_3OEt_2 in chlorinated solvents, the effect of adding tetracyanoethylene, chloranil and 1,3,5-trinitrobenzene was examined.

1.4. Block Copolymers

A block copolymer has been defined[48] as a polymer composed of molecules in which two or more polymeric segments of different chemical composition are attached end to end. Thus, in practice, block copolymers are long sequences of the homopolymeric constituents with comparatively few intersequence linkages (<10). Because the different homopolymeric sequences are generally incompatible with each other e.g. plastic and rubbery and therefore segregate into separate domains, block copolymers possess properties characteristic of the individual components. The term "block copolymer" as used in this thesis does not include graft copolymers, which consist of branched chains pendant from the main polymer backbone.

The nomenclature of block and graft copolymers has been discussed in detail by Ceresa[49]. He proposed (i) that a block copolymer of monomer (M_1) and monomer (M_2) is written in form poly (M_1-b-M_2) and (ii) that some provision be made for the arrangement of segments. This he designated by adopting the letters A,B, etc. to describe the homopolymer sequences[50], which is important since the properties of a block copolymer may be related to the order of the homopolymeric constituents. Examples of such nomenclature are given in equations (1.18-1.21).

ABA poly(M_1-b-M_2) : $M_1 \sim\sim M_1M_2 \sim\sim\sim M_2M_1 \sim\sim M_1$ (1.18)

$(AB)_n$ poly(M_1-b-M_2) : $[M_1 \sim\sim M_1M_2 \sim\sim M_2]_n$ (1.19)

(BAB) poly(M_1-b-M_2) : $M_2 \sim\sim M_2M_1 \sim\sim M_1M_2 \sim\sim M_2$ (1.20)

ABC poly(M_1-b-M_2-b-M_3) : $M_1 \sim\sim M_1M_2 \sim\sim M_2M_3 \sim\sim M_3$ (1.21)

Although the sequences in the block copolymers described in this thesis will usually be apparent from the discussion, this formal notation is used where the structural possibilities are being examined.

Several methods have been used to prepare block copolymers; these include free radical polymerisation, anionic polymerisation, co-ordination catalysts, and step-growth processes. With the exclusion of free-radical methods, all these techniques are only very briefly considered in this thesis. For a general discussion on the processes which may be used to synthesize block copolymeric materials the text edited by Allport and Janes[51], and the review by Bradford and McKeever[52] should be consulted.

1.5. Techniques Employed for the Synthesis of Block Copolymers

1.5.1. Anionic polymerisation

Where applicable, anionic polymerisation provides the most versatile method for the preparation of well defined block copolymers. By utilising the "living" polymer technique consecutive additions of monomer can be made. The homopolymer blocks formed in this way are of specified molecular weights with narrow distributions.

A requirement for preparing an ABA block copolymer by a sequential process is that the anion of each homopolymeric component initiates the monomer of the other. A useful guide to the relative reactivities of the carbanions is recorded by Fetters'[27] classification (TABLE 1.1.). Fetters[2] has studied the various anionic methods available that could be used to prepare thermoplastic-elastomeric materials such as SBS. He lists four different routes to obtain SBS materials, and the first three of these have

general applicability. They are (a) the use of mono-functional initiators in a three stage process, (b) the use of difunctional initiators in a two stage process, (c) the use of mono-functional initiators to form SB blocks which are subsequently coupled, and (d) direct copolymerisation of the two monomers under conditions in which one monomer is polymerised preferentially. The last method (d) is particular to the SBS system.

1.5.2. Co-ordination catalysis

Although co-ordination catalysts have been used mainly in the synthesis of ethylene-propylene[52-55] block copolymers, there are other monomer pairs for which this method of preparation is utilised. Examples include styrene-isoprene[57], ethylene-(but-1-ene)[58], (hex-1-ene)-(4-methylpent-1-ene)[59], and styrene-propylene[60]; a comprehensive list is given in the Allport and Janes text[51].

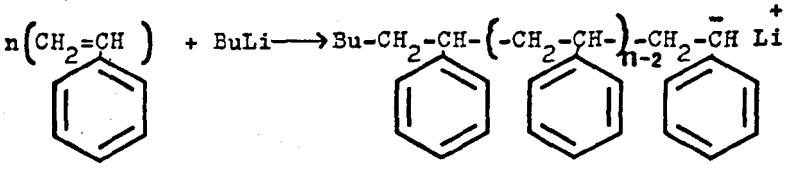
Efficient block copolymer production requires that the co-ordination or Ziegler-Natta catalyst system chosen must be long lived. That is, chain-end lifetimes which vary from minutes to hours are often required, and these have been obtained by the selection of appropriate initiator combinations[61,62].

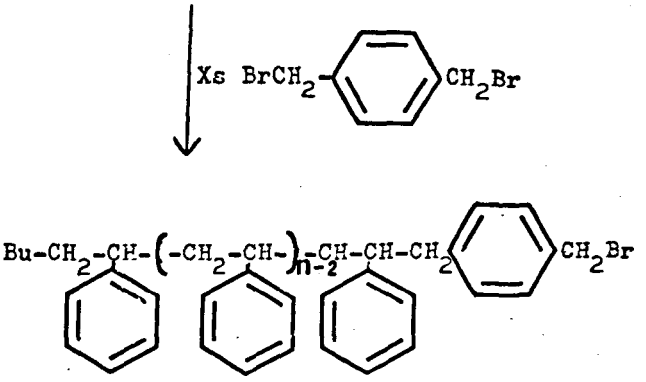
1.5.3. Step-growth processes

A wealth of information has been accumulated on this topic in the form of patents and other scientific publications[63]. Strong commercial interest has promoted the development of block copolymers which possess polyurethane, polyester or polyamide segments. These blocks are linked by condensation reactions, ester exchange reactions or, for the polyurethanes, by reactions which involve addition of diisocyanates to polymeric diols.

As many of the products derived by the step-growth technique contain a large number of polar groups, aggregation into domains occurs at much lower molecular weights than is found for the less polar addition polymers such as polystyrene.

Since co-ordination catalysts and step-growth techniques were not used for the work reported in this thesis, no further discussion of them is given.





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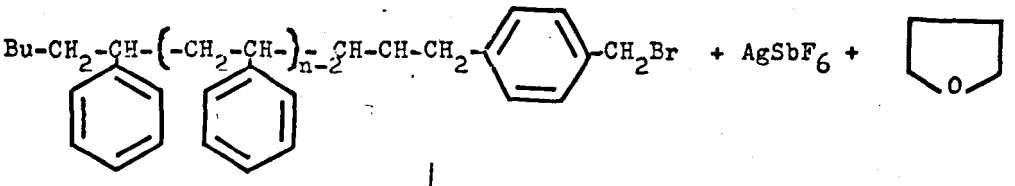

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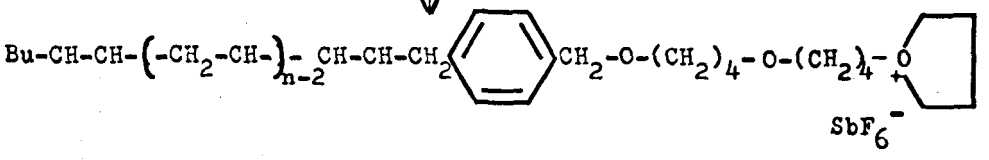


+ AgBr

1.6. *Transformation Reactions*

Anionic polymerisation has proved to be one of the most efficient methods for the production of mono-disperse block copolymers of well defined structure. Its versatility is limited by the relatively small number of monomers capable of being polymerised anionically and the even smaller number of monomer combinations which exhibit reciprocal initiation.

In most monomer combinations, the second monomer can be initiated by the polymeric anion of the first monomer but the resultant anion is then too stable to initiate a fresh aliquot of the first. This situation could be improved and the range of monomers that form block copolymers be increased if the mechanism of propagation could be changed after initial polymerisation of the first monomer anionically, to one best suited for the propagation of the second monomer.

Consider the styrene-THF system, where styrene is polymerised anionically and THF cationically. To obtain an ABA poly(styrene-b-THF) block copolymer the mechanism of propagation would have been changed.

The steps to effect such a transformation would involve:
(1) the polymerisation of styrene by an anionic mechanism and the conversion of the polystyryl anion into a metastabe state (equation (1.2 1.a.));
(2) isolation of the stabilised polystyrene, its dissolution in a suitable solvent for cationic polymerisation, addition of THF;
(3) the reaction, or change of conditions, to transform the stabilised end of the polystyrene into a propagating species which will polymerise THF by cationic mechanism (equation (1.2 2.)).

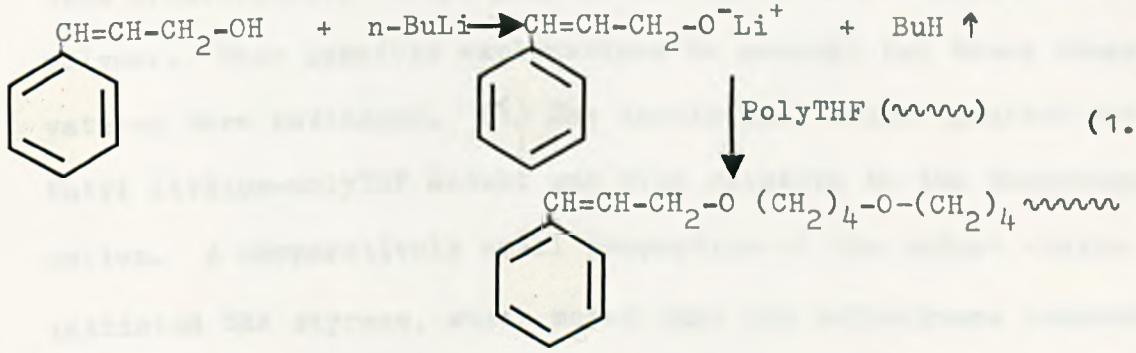
The intermediate polymer should be stable enough to allow isolation and should have a storage lifetime of about one month.

The criteria outlined above have been used to develop methods of effecting cationic to anionic[64], anionic to cationic[10] and anionic to free radical[11] transformations. A recent study has been undertaken on a cationic to anionic transformation; and an account of that work is given in this thesis.

1.6.1. Cationic to anionic transformation

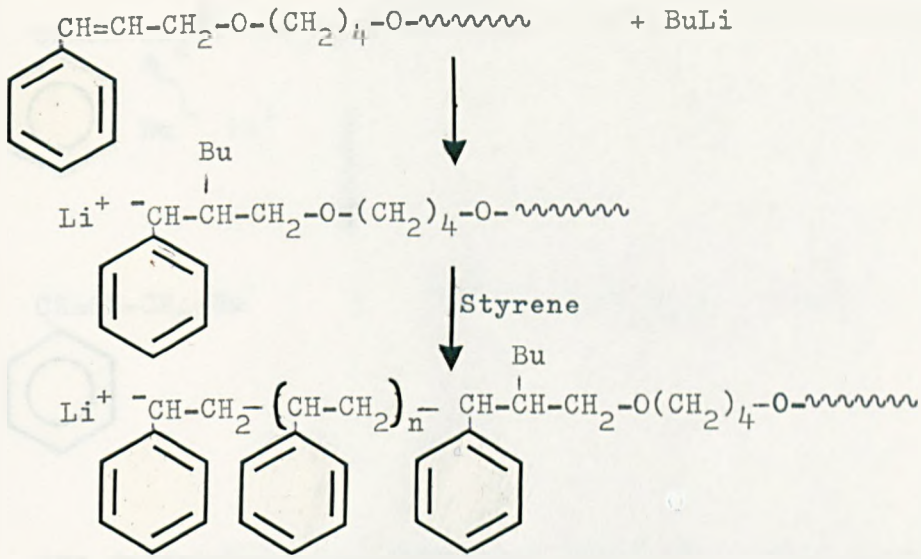
A system in which propagating cationic chains are transformed to polymerise monomers by an anionic mechanism was examined.

Exploratory work was completed in Richards' laboratories at Waltham Abbey, before the present study had commenced and involved the use of cinnamyl alkoxide as a terminating agent for living polyTHF. The alkoxide proved to be a very efficient terminating agent (equation (1.23)) ; the percentage of living chains capped was >95% although cinnamyl alcohol itself was found not to react rapidly or quantitatively with living polyTHF.



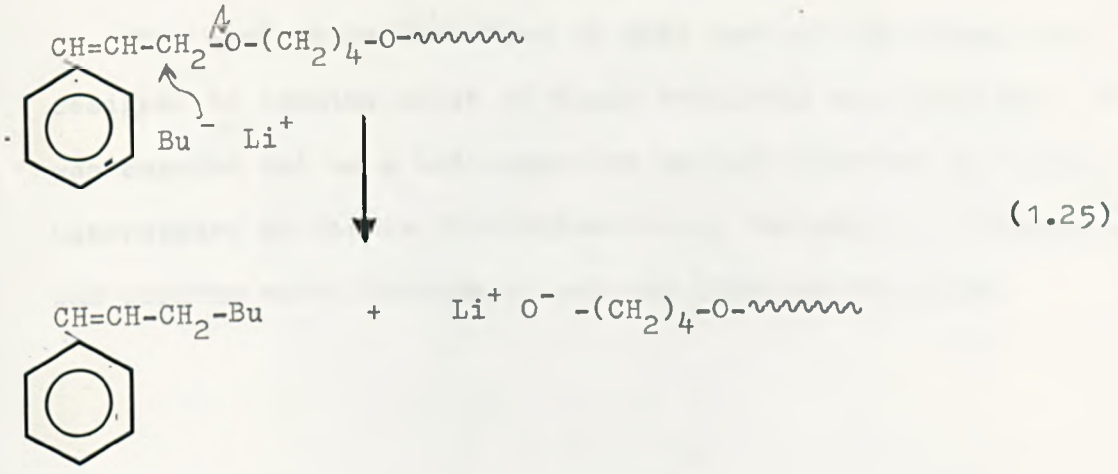
(1.23)

It was recognized that the terminal adduct was possibly analogous to a β-substituted styrene unit. Consequently, it was hoped that reaction with butyl lithium would result in addition across the vinyl double bond to form a substituted benzylic anion which could be used to propagate suitable monomers, for example styrene, to form block copolymers (equation (1.24)).



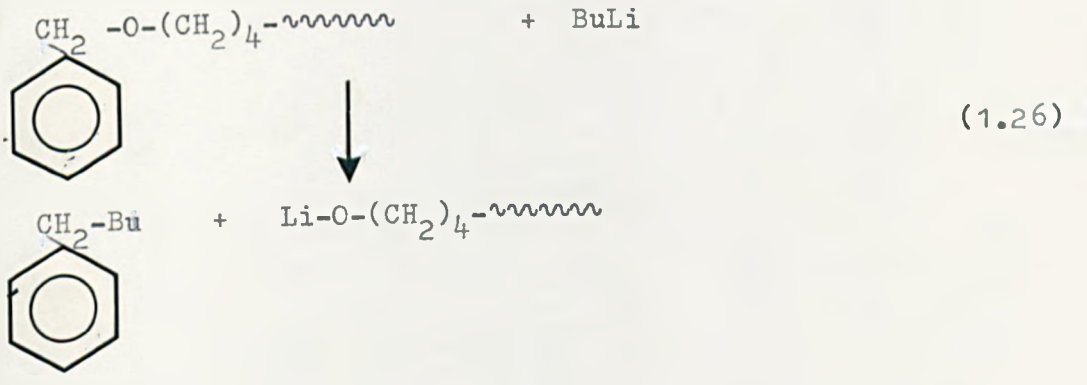
(1.24)

However, preliminary experiments showed that the polystyrene component of such a reaction sequence had a molecular weight significantly higher than that predicted by the stoichiometry of the reagents. Further, there was suspicion that the high molecular weight polystyrene component of the product could have been predominantly homopolymer rather than the desired block copolymer. Four possible explanations to account for these observations were envisaged. (1) The initiation, which involved the butyl lithium-polyTHF adduct was slow relative to the homopropagation. A comparatively small proportion of the adduct chains initiated the styrene, which meant that the polystyrene component of the block attained a correspondingly higher molecular weight. (2) The addition of butyl lithium to the polyTHF was not quantitative and the superior reactivity of unreacted butyl lithium resulted in homopolystyrene being formed. (3) The butyl lithium may have been consumed by reaction with the polyTHF terminal groups through an alternative scission process which could involve attack at the terminal allylic ether group (equation (1.25)).



(1.25)

The ß-pentylstyrene generated could then react with a further molecule of butyl lithium to form an initiator for polymerisation of styrene. (4) Since benzyl bromide was used as an initiator with $AgPF_6$ for the polyTHF, addition of the first monomer unit results in the formation of a benzylic ether which is also susceptible to cleavage by butyl lithium (equation (1.26)).



(1.26)

Of course these possibilities are not mutually exlusive, and the correct explanation may involve a combination of these individual reactions.

The work to be described in this part of the thesis was designed to examine which of these reactions was important, and was carried out as a collaborative project with Mr. T. Souel, Laboratoire de Chemie Macromoleculaire, Montpellier, France, who was working with Richards at Waltham Abbey at the time.

References to CHAPTER 1.

1. M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes", Interscience, New York, 1968.
2. L.J. Fetters, J. Elastoplastics, 1972, 4, 34.
3. D.H. Richards and M. Szwarc, Trans. Faraday Soc., 1959, 55, 1644.
4. M.P. Dreyfuss and P. Dreyfuss, Polymer, 1965, 6, 93.
5. T.G. Croucher and R.E. Wetton, Polymer, 1976, 17, 205.
6. G. Berger, M. Levy and D. Vofsi, J. Polym. Sci., (B) 1966, 4, 183.
7. F.J. Burgess, A.V. Cunliffe, D.H. Richards and D. Thompson, Polymer, to be published.
8. D.H. Richards, S.B. Kingston and T. Souel, Polymer, 1978, 19, 68.
9. D.H. Richards, S.B. Kingston and T. Souel, Polymer, 1978, 19, 806.
10. F.J. Burgess, A.V. Cunliffe, J.R. MacCallum and D.H. Richards, Polymer, 1977, 18, 719.
11. T. Souel, F. Schue, M. Abadie and D,H, Richards, Polymer, 1978, in press.
12. C.H. Harries, Ann., 1911, 385, 184. U.S, Pat, 1,058,056., 1913.
13. F.E. Matthews and E.H. Strange, Brit. Pat., 24,790 1910.
14. W. Schlenk and E. Bergmann, Ann., 1928, 464, 1.
15. W. Schlenk, J. Appenrodt, A. Michael and A. Thal, Ber., 1914, 47, 473.
16. N.D. Scott, J.F. Walker and V.L. Hansley, J. Amer. Chem. Soc., 1936, 58, 2442.
17. K. Ziegler and H. Kleiner, Ann., 1929, 473, 57.

18. K. Ziegler and F. Dersch and W. Wollthau, Ann., 1934, 511, 13.

19. K. Ziegler and L. Jakob, Ann., 1934, 511, 45.

20. K. Ziegler, L. Jakob, H. Wollthau and A. Wenz, Ann., 1934, 511, 64.

21. K. Ziegler, Angew Chem., 1936, 49, 499.

22. M. Szwarc, Nature, 1956, 178, 1168.

23. R. Milkovich, M. Levy and M. Szwarc, J. Amer. Chem. Soc., 1956, 78, 2656.

24. H.W. McCormick, J. Polym. Sci., 1957, 15, 488.

25. M. Szwarc, Makromol. Chem., 1960, 35, 132.

26. D.H. Richards, "Anionic Polymerisation" in Press.

27. L.J. Fetters, J. Polym. Sci., C, 1969, 26, 1.

28. E. Franta and P. Rempp, C.R. Hebd.Seanc.Acad.Sci.Paris, 1972, 254, 674.

29. A.W. Mayer, R.R. Hampton and J.A. Davison, Rubber Chem. Technol., 1953, 26, 522.

30. A. Rembaum, F.R. Ells, R.C. Morrow and A.V. Tolbolsky, J. Polym. Sci., 1962, 61, 155.

31. W. Cooper and G. Vaughan, Progress in Polymer Science, (ed. A.D. Jenkins), 1967, 1, 93.

32. J.I. Cunneen, G.M.C. Higgins and W.F. Watson, J. Polym. Sci., 1959, 41, 1.

33. H. Brody, D.H. Richards and M. Szwarc, Chem. and Ind., LONDON, 1959, 1473.

34. D.H. Richards and N.F. Scilly, Chem. Comm., 1968, 23, 1515.

35. G. Williams, J. Chem. Soc., 1938, 246.

36. P.H. Plesch, (ed.), "The Chemistry of Cationic Polymerisation", Pergamon Press, 1963.

37. P.H. Plesch, "Cationic Polymerisation", Progress in High Polymers, 1968, 2, 137.

38. H. Meerwein, D. Delfs and H. Morschel, Angew. Chem., 1960, 72, 927.

39. P. Dreyfuss and J.P. Kennedy, J. Polym. Sci., 1976, Symposium No. 56, 129.

40. D. Dunn, Polymer J., 1976/77, 8, 67.

41. P. Kubisa and S. Penczek, Makrom. Chem., 1969, 130, 186.

42. P. Dreyfuss and M.P. Dreyfuss, Adv. Polym. Sci. 1967, 4, 528.

43. B.A. Rosenberg, E.B. Ludvig, A.R. Gantmakher and S.S. Medvedev, J. Polym. Sci. (C) 1967, 16, 1917.

44. A. Ledwith and D.C. Sherrington, "Reactivity, Mechanism and Structure in Polymer Chemistry", (Eds. A.D. Jenkins and A. Ledwith), Wiley, LONDON, 1974, Ch.9.

45. P. Dreyfuss, J. Macromol. Sci., (A), 1973, 7, 1361.

46. P.H. Plesch, "Cationic Polymerisation", Consiglio Nazionale Della Ricerche, 1963.

47. I.M. Panayotov , I.K. Dimitrov and I.E. Bakerdjier, J. Polym. Sci., (A1), 1969, 7, 2421.

48. M.L. Higgins, P. Corradini, V. Desreux, O. Kratky and H. Mark, Polymer Letters, 1968, 6, 257.

49. R.J. Ceresa, "Block and Graft Copolymers" Butterworths, LONDON 1962.

50. Papers in J. Polym. Sci., (C), Polymer Symposia, 1969, 26.

51. D.C. Allport and W.H. Janes, "Block Copolymers" Applied Science, LONDON 1973.

52. E.B. Bradford and L.D. McKeever "Progress in Polymer Science" Pergamon Press, (Ed. A.D. Jenkins), 1971, 3, 145.

53. G.E. Ham, (ed.) "Copolymerisation", Interscience, NEW YORK, 1964.

54. G. Bier, G. Lehmann and H. Leugering, Makromol. Chem., 1961, 44, 347.

55. E.G. Kontos, E.K. Easterbrook and R.D. Gilbert, J. Polym. Sci., 1962, 61, 69.

56. E. Junghanns, A. Gumboldt and G. Bier, Makromol. Chem., 1962, 58, 18.

57. N.G. Gaylord, B. Matyska, I. Kossler and H. Krauserova, Polymer, Preprints, 1967, 8, 830.

58. Brit. Pat. 1,094,838, 1965.

59. Brit. Pat. 1,093,344, 1965.

60. G.A. Razuroyev, K.S. Minsker and I.Z. Shapiro, Vysomolekul., Soedin, 1962, 4, 1833.

61. G. Natta and J. Pasquon, Adv. Catalysis, 1959, 11, 1.

62. G. Natta, J. Polym. Sci., 1959, 34, 531.

63. G. Odian, "Principles of Polymerisation", McGraw-Hill, 1970.

64. J.P. Kennedy and E.G. Melby, J. Polym. Sci. 1975, 13, 59.

CHAPTER 2

EXPERIMENTAL

2.1. Materials

Checks on the purity of reagents were made by g.l.c. at the start of the work. However, once it was established that the purity levels >95% were consistently obtained, the checks were discontinued.

Styrene and α-methylstyrene (British Drug Houses Ltd.) were dried over calcium hydride and distilled under reduced pressure before use (boiling range 315-318K for styrene and 335-339K for α-methylstyrene at 0.1mm Hg).

Tetrahydrofuran (THF), stabilised with 0.1% quinol, (B.D.H.Ltd.) was always distilled freshly into the reaction flask under nitrogen after sufficient 0.7M sodium naphthalene solution had been added to produce a permanently green solution. The sodium naphthalene solution was prepared by rapidly stirring "purified" naphthalene (12.8g, 0.1 mole) with 1mm diameter sodium wire (4g, 0.2 mole) in distilled THF for 45 minutes, under nitrogen. This quantity was normally more than sufficient for 2 litres of THF. The sodium naphthalene radical anion reacts with all impurities, principally water and the stabiliser, which would cause termination of the polymeric carbanions.

Analar benzene (B.D.H. Ltd.) was the solvent used for the preparation of monofunctional polystyrene. It was distilled azeotropically in the reaction vessel. This served to remove water from the benzene and to dry the flask (reaction vessel).

n-Butyl lithium was purchased from Aldrich Chemical Co. Ltd. as a 1.6M solution in hexane and was stored in a refrigerator at 258K. Contact with the air was minimized. A Gilman titration[65] was carried before use to ascertain the exact molarity.

Silver hexafluorophosphate (Pfaltz and Bauer) and silver hexafluoroantimonate (Ventron Alfa Products) were supplied as free flowing powders and used without further purification but were always stored under nitrogen.

α,α'-Dibromoxylene (referred to hereafter as xylylene dibromide). The para isomer (Koch-Light) was recrystallised from benzene before use.

Benzyl bromide (B.D.H. Ltd.) was distilled and stored over molecular sieves.

Analar pyridine (B.D.H. Ltd.) was dried over calcium hydride and distilled before use.

1,1-Diphenylethylene (Aldrich Chemical Co. Ltd.) was distilled before use (423K at 1.0 mm Hg).

Analar bromine (B.D.H. Ltd.) was used as supplied.

Cinnamyl alcohol (Aldrich Chemical Co. Ltd.) was distilled before use.

1,2-Dibromoethane (B.D.H. Ltd.) was distilled before use (294K at about 1.0 mm Hg).

Magnesium turnings (B.D.H. Ltd.) only "clean" i.e. brightly coloured turnings were used.

Calcium hydride (B.D.H. Ltd.) large quantities were used in the work, it was always freshly ground under a stream of nitrogen.

Methanol (B.D.H. Ltd.) commercial grade, was used as supplied.

Nitrogen (British Oxygen Company Ltd.) "White spot", oxygen-free nitrogen was always used.

2.2. Apparatus

Conventional glassware with ground-glass joints was used. Special equipment was constructed, e.g. the burette in Figure 2.2. and the transfer tubes with filter thimbles of different porosities, Figures 2.7. and 2.8.

The apparatus received a routine but meticulous cleaning treatment before any reaction or preparation was attempted. The treatment comprised several washings, starting with chromic acid, followed by copious quantities of de-ionised water, and finally Analar acetone (B.D.H. Ltd.) and Analar chloroform (B.D.H. Ltd.), before drying for 24 hours at 393K. Only glassware the internal surfaces of which were seen to be completely wetted by water in the rinsing stage, was considered to be sufficiently clean for use. Each of the washings had its own characteristic procedure, e.g. with chromic acid, the apparatus was totally immersed in an acid bath for periods of up to six hours. The apparatus was then removed and rinsed rapidly with fresh acid before being washed with water.

Apparatus (Figure 2.2.) which was only partly cleansed in that manner received additional cleaning which entailed flaming out under nitrogen, before use. The syringes used for the introduction of reactants into the reaction vessel, received the full washing and drying treatment. The needles were cleaned with a wire to remove large particles and then washed with acetone and dried for 24 hours at 393K.

"Subaseal" rubber septum stoppers supplied by Gallenkamp Ltd. were employed when access to a reaction vessel by a syringe was necessary.

Drechsel gas washing bottle heads (Quickfit MF 28/2) were used as nitrogen inlet/outlets.

2.3. Procedures for Preparing Living Polymers

It was of prime importance that the living polymeric systems used in the work should have been prepared in the most effective way possible since the efficiency of formation of block copolymers is directly related to the purity of the initiating polymers. Each preparation was therefore planned carefully and every precaution was taken to ensure a high standard of purity of the reagents and cleanliness of the apparatus. Trial runs were carried out in order to become familiar with the processes involved and to note the difficult features associated with the preparation. Thus, when the actual preparation was completed it had been preceded by careful exploratory work.

Since water is an ubiquitous impurity causing virtually instantaneous termination of the living anion or cation, it was essential for no significant amounts to be present in the reaction mixture. The procedure designed to minimize its presence in apparatus outlined in section 2.2. was followed in each case as were the procedures given in section 2.1. for purifying the solvents, monomers and other specific reagents. Similarly, any oxygen present terminates carbanions so preparations were always conducted under nitrogen. It was general practice to carry out procedures involving the handling of "dry" materials, such as the weighing out of the silver salts for the polyTHF preparations under a continuous stream of nitrogen.

Since all the preparations utilized different practical points of importance it is therefore appropriate to record systematically the salient features of each before describing the preparation in detail.

The molarities of the polymer solutions are expressed in moles per litre of living ends.

2.3.1. Polystyryl lithium (Molecular Weight 20,000)

Addition of the initiator, butyl lithium, to a cooled benzene styrene solution produced a yellow colouration. The yellow colour turned to a clear red on addition of THF (a good solvating agent) and rapid polymerisation of the styrene ensued. The deepening of the colour is undoubtedly connected with dissociation of the styrene oligomers, known to exist as dimers in benzene, and the solvation of the resulting monomeric species by THF.

This method is a modification of a high vacuum technique described in the literature[66].

Before assembling the apparatus as in Figure 2.1. the polymerisation flask was charged with benzene (280ml) which was then purified in the following manner. The flask was fitted with a Dean and Stark apparatus, with a calcium chloride guard tube fitted to the top of the condenser. The benzene was boiled under reflux and any water present was removed in the "wet" benzene fraction (30ml) collected in the arm of the Dean and Stark apparatus. The dry benzene was cooled under a slow stream of nitrogen before the apparatus in Figure 2.1. was assembled. For all the figures in this Chapter the letter "S" is meant to denote a subaseal.

The benzene (250ml) was stirred vigorously while styrene (23ml, 0.2 mole) was added from a syringe, the mixture was then cooled to a slurry by an ice/salt bath. It was necessary to stir the styrene solution at about 900 r.p.m. during this process to avoid the benzene freezing onto the flask walls. Whilst maintaining

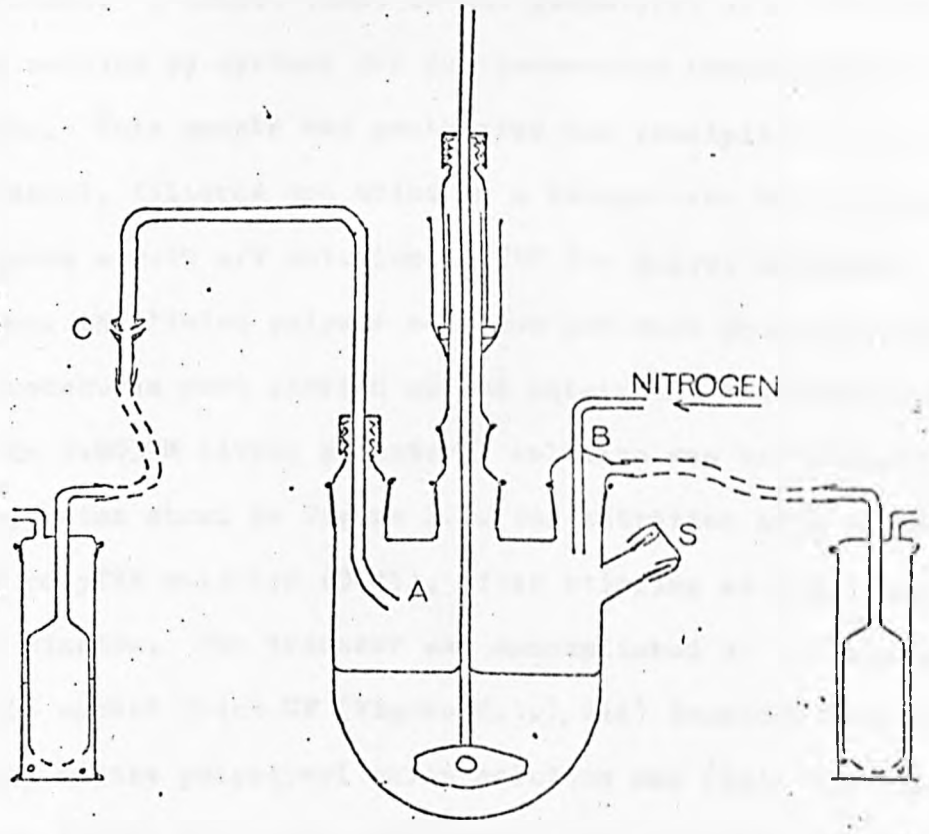


FIGURE 2.1. AN APPARATUS USED FOR THE PREPARATION OF LIVING POLYMER.

the rate of stirring consecutive additions of butyl lithium (0.65ml, 0.001 mole) and THF (3ml), both by syringes, were then made with a time interval of 30 seconds. A faint yellow colour diffused through the slurry on addition of the butyl lithium. This was due to the slow initiation of styrene in benzene. On addition of the THF an immediate red resulted which indicated the formation of the living polystyryl anion. The heat of polymerisation melted the slurry and the solution was stirred for 30-45 minutes at room temperature. A sample (5ml) of the polystyryl anion solution was always removed by syringe for gel permeation chromatography (g.p.c.) analysis. This sample was protonated and precipitated by addition to methanol, filtered and dried in a vacuum oven before being used to prepare a 0.1% w/v solution in THF for g.p.c. analysis.

Once the living polymer solution had been produced, individual procedures were carried out to obtain the required product.

The 0.0037M living polystyryl solution was transferred to the apparatus shown in Figure 2.2. for titration into the 0.01M living polyTHF solution (90ml), after stirring at room temperature for 45 minutes. The transfer was accomplished by (i) connecting the ball socket joint CF (Figure 2.1.), (ii) lowering tube A into the body of the polystyryl anion solution and (iii) blocking the nitrogen outlet B to force the liquid up A into the burette.

2.3.2. Difunctional polystyryl sodium (Molecular Weight 5,000)

Preparation of difunctional polystyrene involved several stages which required delicate procedures. For example, careful regulation of nitrogen pressure was necessary to avoid forcing unpurified THF prematurely out of the reaction vessel and into the flask which was to be used for the initiator preparation (Figure 2.3).

See FIGURE 2.1.

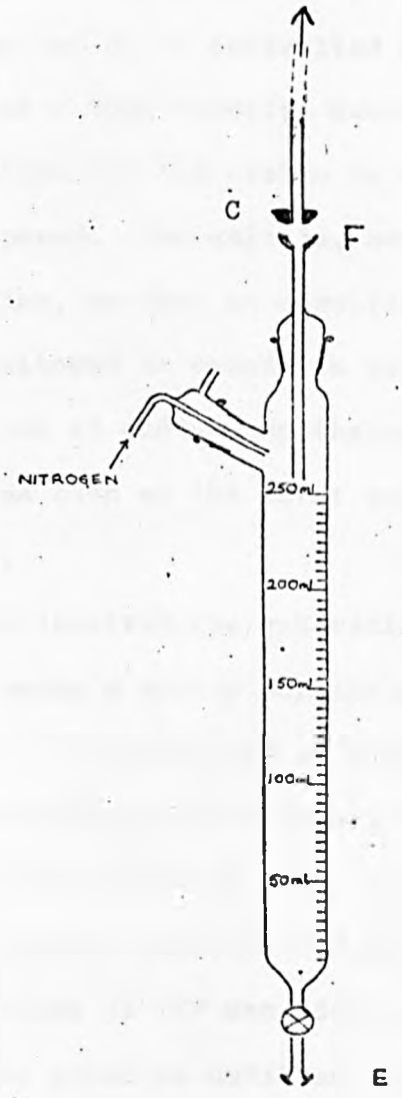


FIGURE 2.2. BURETTE FOR TITRATING LIVING POLYMER SOLUTION INTO TERMINATING AGENT

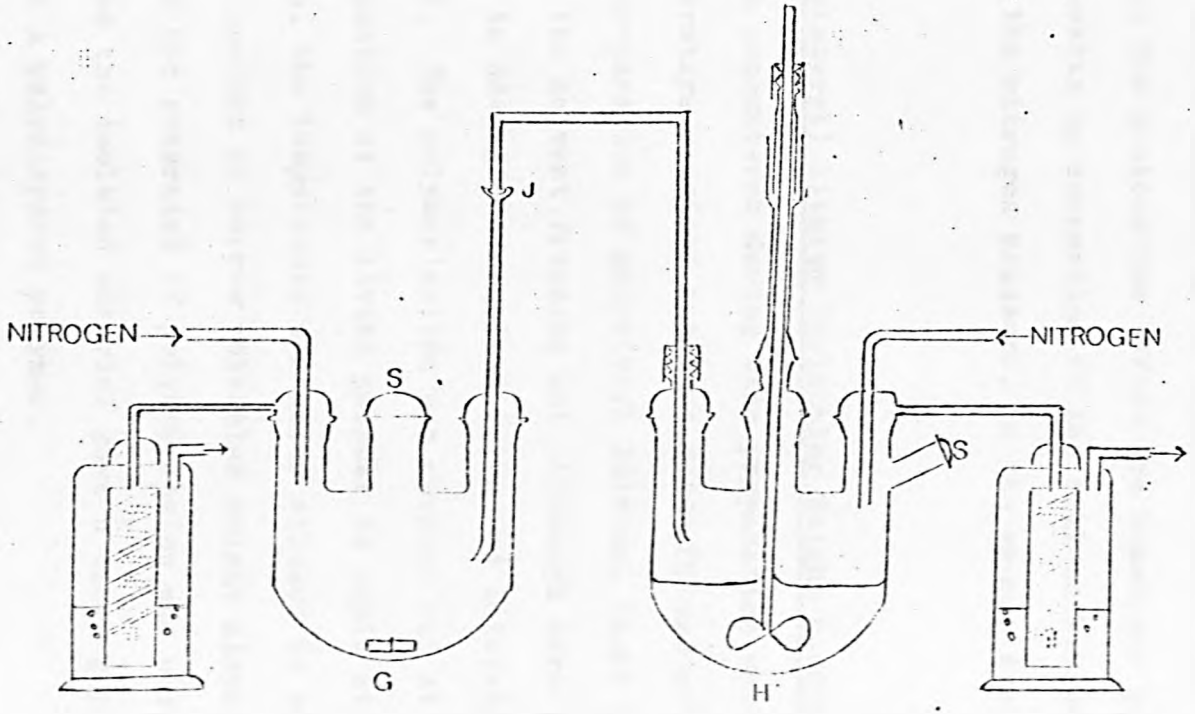
Had this occurred it would have resulted in significant contamination of the catalyst system. Similarly, the subsequent purification of the THF solvent by the dropwise addition of the sodium naphthalene solution had to be controlled carefully. Because sodium naphthalene is a very reactive nucleophile it is an ideal scavenger of impurities for the system in which the polystyryl sodium is to be prepared. The salt is, however, an initiator of styrene polymerisation, so that no significant excess of sodium naphthalene can be allowed to remain in the purified THF. Therefore the slow addition of sodium naphthalene to the solvent was halted immediately as soon as the first permanent faint green colour was observed.

The preparation involved the generation of a dicarbanion. This was formed by using a sodium naphthalene (NaN) solution (1.00M) in THF as initiator. The apparatus is shown in Figure 2.3. and the procedure was as follows. The system was flushed with nitrogen, purified THF (250ml) was added to flask G, and by careful regulation of the nitrogen flow no THF was forced over into flask H. To that volume of THF was added dropwise the sodium naphthalene initiator solution until an extremely faint green colour was produced. Styrene (23ml, 0.2 moles) was added slowly from a syringe into flask G. A sample of this monomer solution was then withdrawn (by syringe) and injected into methanol as a check to see if any polymerisation had ensued as a result of excess NaN having been added.

A few drops of the initiator solution were added to the clean empty flask H until a green colour remained. This removed any last traces of impurities from the flask, after which an aliquot (10ml, 0.01 moles) of the initiator was added and H placed in an

FIGURE 2.3.

APPARATUS FOR THE PREPARATION OF DIFUNCTIONAL LIVING POLYMERS.



ice/salt bath. The styrene solution was then transferred from flask G, by nitrogen pressure, into the rapidly stirred initiator solution in flask H. A dark cherry red solution was obtained; which was indicative of the polystyryl anion. The 0.0353M living solution was stirred for 30 minutes in an ice/salt bath, then a 5ml sample was removed for protonation before the remainder was transferred to the burette by connection of the ball-socket joint JF and regulation of the nitrogen pressure, in the manner described in section 2.3.1.

2.3.3. Poly(α-methylstyryl) lithium (Molecular Weight 6,000)

The main problem encountered during this preparation was to ensure that the temperature remained constant. Since THF and not benzene was used, unlike in the preparation of polystyryl lithium, there were no difficulties with the solvent freezing out, although care had also to be exercised in adding the required volume of initiator to obtain the desired DP. The polymerisation was carried out at 195±2K; as depolymerisation of the living polymer is rapid at more elavated temperatures, the temperature was never allowed to exceed 210K. The polymeric product of narrow molecular weight dispersity formed below 200K was not generated if polymerisation was undertaken at 250K; instead the isolated material gave a broad g.p.c. trace which indicated a polydisperse polymer.

THF was distilled under nitrogen into the burette (Figure 2.2.) and the required volume (250ml) run directly into the reaction flask (Figure 2.1.). α-Methylstyrene (30ml, 0.233 mole) was added by syringe, with rapid stirring. The mixture was then cooled to 195K using an isopropanol/cardice bath, before the addition of butyl lithium (3.2ml, 0.005 mole) was made from a syringe.

An immediate deep red colour was formed; this is characteristic of the poly (α-methylstyryl) anion. The red solution was left to react for 30-45 minutes at 195K. A sample (5ml) was withdrawn for g.p.c. analysis and treated in the same way as reported for the polystyryl lithium (section 2.3.1.). The remainder of the poly (α-methylstyryl) anion solution was transferred to the burette by the method outlined in section 2.3.1. for titration to the living polyTHF solution.

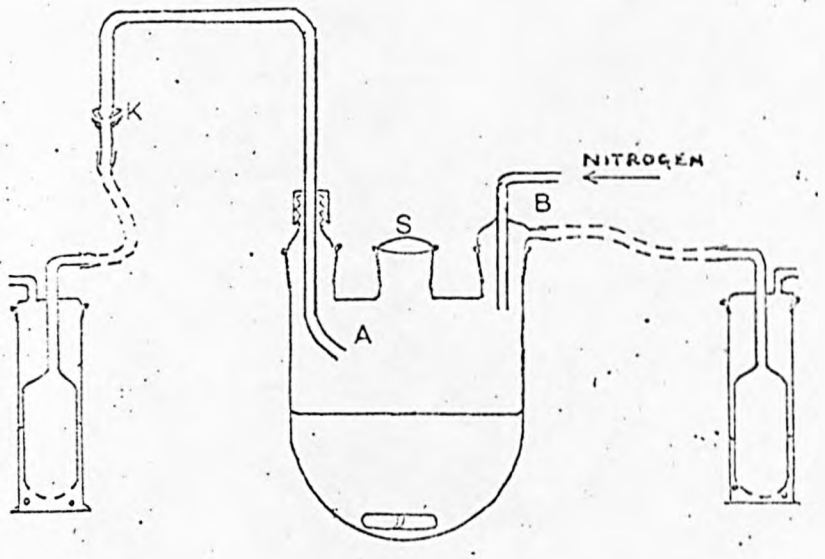
2.3.4. α-Methylstyrene tetramer

The method to be described was adapted from a high vacuum technique described in the literature[3,67]. α-methylstyrene (11.8g, 0.1 mole) was weighed directly into a 250ml round-bottom, three-necked flask and THF (150ml) was added to make a 0.167M tetramer solution. An approximately two-fold excess of sodium metal (2.3g, 0.1 mole) was pressed into the α-methylstyrene THF solution as 2mm diametre wire. The flask was fitted with a magnetic stirrer, septum cap, nitrogen inlet and transfer tube (Figure 2.4.) which was connected to the burette by ball-socket joint KF when forcing the tetramer solution into the burette.

As the sodium wire entered the solution a deep red colour appeared on its surface which permeated into the body of the solution after stirring it rapidly for a minute or so. Once the solution had turned red, the rate of stirring was kept low (∿100 r.p.m.) for two hours. (The rate of reaction is known to be diffusion controlled[68] and is therefore related to the rate of stirring, the concentration of monomer and the surface area of the sodium. The conditions used in the experiment are an optimum balance of these variables if depropagation of the tetramer in the

FIGURE 2.4.

APPARATUS FOR THE PREPARATION OF LIVING ∝-METHYLSTYRENE TETRAMER



presence of excess sodium to give dimer and trimer is to be avoided)[69]. A sample was removed with a syringe, protonated by methanol and submitted to g.p.c. and g.l.c. analysis. By means of a temperature programme of 423-573K at 12° rise per minute, it was possible to show by comparison with an authentic sample that tetramer had been formed with only a trace of residual monomer present; g.p.c. supported this evidence. The living tetramer solution was then cooled to 195K by a cardice/isopropanol bath before transferring it into the burette.

2.3.5. Monofunctional polytetrahydrofuran (Molecular Weight 10,000)

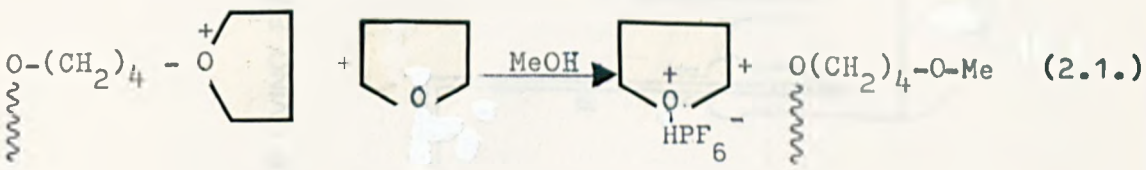
The absence of significant proton transfer reactions during the polymerisation of THF enabled polymers possessing terminal cations, either monofunctional or telechelic to be prepared under "living" conditions.

Although synthesis of the polymer was straight forward, certain precautions were observed to prepare both mono- and difunctional living polyTHF of narrow poly dispersity with equal facility. It was important that all reagents were as dry as possible. Water can react with the propagating cationic chains to terminate them with hydroxyl groups and regenerate the corresponding acid which in turn acts as an initiator. By this process "dead" oligomeric or polymeric polyTHF chains can be created which cannot participate in any linking reactions to be carried out subsequently. To avoid this, the hygroscopic silver salts were stored in a desiccator before use and were manipulated under dry nitrogen.

The rate of propagation is temperature-dependent and monofunctional initiators with the PF_6^- counter ion were found to yield polymers of approximately 5,000 molecular weight (polystyrene equivalent) after polymerisation at 263K for one hour. Removal of the silver bromide by passage through a filter stick (of varying porosity, depending on molecular weight of the polymer formed), was routine in all the polyTHF preparations. This proved to be the most difficult operation encountered throughout the work. Two techniques of filtration were tried: The first involved forcing the silver bromide/polyTHF solution up the open end of the transfer tube, thus collecting the silver bromide in the sintered bulb at the other end (Figure 2.5.). The second method was the reverse of the first in which the sintered bulb was kept in the solution awaiting filtration. The second method proved to be the more effective for the following reasons: (i) the polymeric solution remained at 263K throughout the transfer, whereas in the first method warming of the solution in the transfer tube could occur should the sintered bulb become blocked and so prevent passage of the liquid, (ii) the filtration was quicker because a larger outer surface area of the filter bulb was available to the total volume of solution. The effectiveness of the process was later improved by adopting the following technique: A strong nitrogen pressure was applied until the bulb became coated with precipitate so that the volume of clear liquid being collected only increased very slowly. This pressure was then suddenly released, which caused the silver bromide on the bulb to be dislodged and the unfiltered solution in the transfer tube to return rapidly to its flask drawing the precipitate with it. By re-application of a strong nitrogen pressure another aliquot was brought onto the sinter, filtered

and collected. This "off-on" nitrogen pressure technique was capable of filtering 90 ml of 0.01M solution of a 10,000 molecular weight polymer within 10 minutes. Stopping the stirring of the polyTHF solution before filtering to allow the silver bromide to settle made little difference to the time of filtration.

As outlined in section 2.6., if the g.p.c. instrument was occupied by other users then a series of brine-ether extractions was carried out on the isolated polyTHF samples. The reason for this procedure is that during the reaction with methanol a PF_6^- acid complex is generated (equation (2.1.)).



(2.1.)

The acid is able to initiate polymerisation and also to induce chain scission.

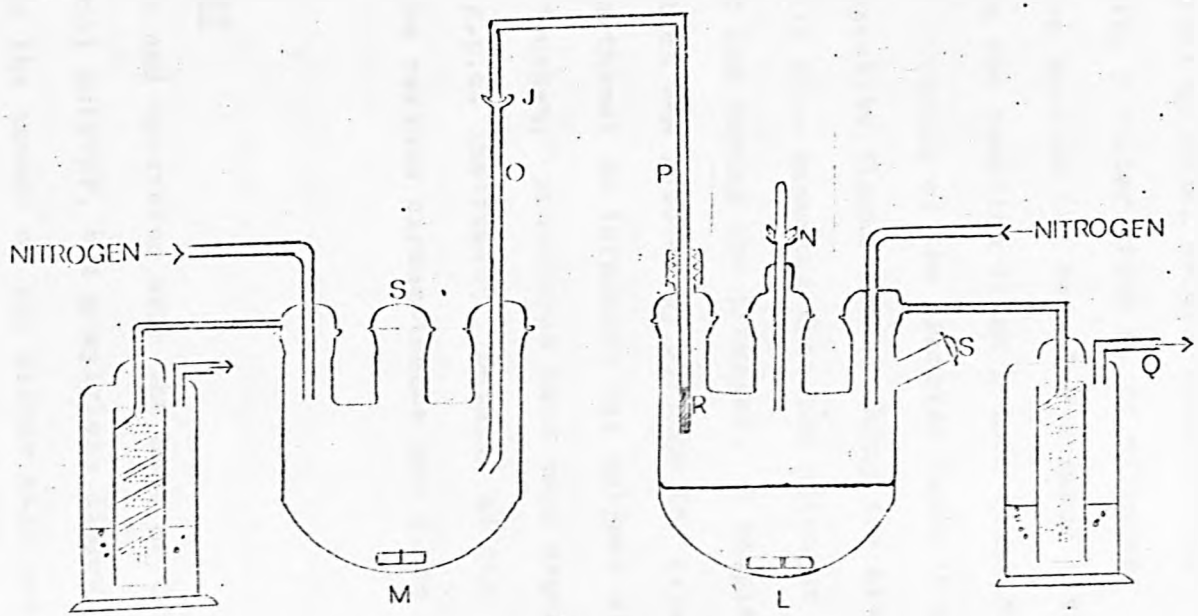
PolyTHF samples that did not undergo any brine-ether extractions were found by g.p.c. to have broad molecular weight distributions, while those samples which received the brine-ether treatment had narrow molecular weight distribution.

Experimental conditions for the preparation of "living" polyTHF of narrow molecular weight distribution have been reported in the literature[5] and were complied with in the following method.

A 0.01M living polyTHF solution (100ml) was prepared with apparatus shown in Figure 2.5. THF was distilled into the burette (Figure 2.2.) under nitrogen, and the required volume (95ml) was

FIGURE 2.5.

APPARATUS FOR THE PREPARATION OF LIVING POLY THF.



run into the reaction vessel. The rapidly stirred THF was cooled to 263K before a THF solution (5ml) of silver hexafluorophosphate (0.275g, 1.1 mole) was added by syringe. Addition of benzyl bromide (0.12ml, 1 mole) caused the precipitation of cream coloured silver bromide. The reaction was allowed to proceed for two hours at 263K, before transferring the solution through a porosity 3 filter stick R, by nitrogen pressure, to remove the silver bromide and so allow a clear living polyTHF solution to pass from the reaction flask L into flask M. This was accomplished by the lowering of the transfer tubes O and P to the bottom of their respective flasks and blocking the nitrogen outlet Q of flask L, while also ensuring that the nitrogen pressure in flask M was kept low during the transfer. A sample (20ml) of the filtered solution was removed by syringe for g.p.c. analysis and injected into methanol to terminate the polymer with methoxy groups. Different "work-up" procedures were used depending on the availability of the g.p.c. instrument. Details of the isolation procedure under the various circumstances are given in section 2.6.1.

2.3.6. Difunctional polyTHF

The reaction procedure and apparatus were the same as for the preparation of monofunctional polyTHF, but p-xylylene dibromide was the initiator and twice the amount of the silver salt was therefore required. A filter stick of porosity 2 rather than 3 was needed when polymerising THF to high molecular weights; this applied equally to the monofunctional PTHF system.

2.4. Reactions of Living Polymers to give Reactive End Groups

2.4.1. Reaction of polystyryl lithium with bromine

The bromine terminated polystyrene was prepared for use in the cationic to anionic transformation study with polymers. A solution of polystyryl lithium of 2,000 M.W. was prepared and transferred to the burette as described in section 2.3.1.

Analar benzene (100ml) was refluxed in a 500ml four necked, round-bottom flask with a Dean and Stark apparatus to remove a fraction (30ml) containing any traces of water. The dry benzene was allowed to cool under nitrogen while the flask was fitted with a magnetic stirrer, a nitrogen inlet, a delivery tube drawn out to a capillary (1mm) and a socket which was attached to the ball joint C of the burette in Figure 2.2. In the fourth neck of the reaction flask was a subaseal. A twenty-fold molar excess of bromine (10ml, 0.2 mole) over the polystyryl chains was added to the benzene by syringe. The polystyryl lithium solution was then run into this vigorously stirred bromine solution from the burette. When the addition was completed, the excess of bromine was removed with a sodium thiosulphate solution containing crushed ice. The now colourless reaction mixture was separated from the aqueous layer and was washed several times with brine and filtered to remove the sulphur formed by reaction with the thiosulphate. Finally the polymer was precipitated in methanol (2 litres). The polymer was analysed by g.p.c.

2.4.2. Reaction of poly(α-methylstyryl) lithium and di-sodium α-methylstyryl tetramer with magnesium bromide

Since it was essential that no impurities were present in the reagents used with the living polymers the anhydrous solution of the magnesium bromide in THF was prepared "in situ"[70,71]. The gradual addition of 1,2-dibromoethane (18.5g, 0.1 mole) to magnesium turnings (3g, 0.125 mole) in refluxing THF (350ml) in the apparatus shown in Figure 2.6. was a highly exothermic process. Very rapid stirring was necessary to prevent uncontrolled frothing due to this exothermic reaction (equation (2.2.)):

$$Mg + Br\text{-}CH_2\text{-}CH_2\text{-}Br \longrightarrow MgBr_2 + \dot{C}H_2 = CH_2 \uparrow \qquad (2.2)$$

The reaction was carried out under nitrogen and a liquid paraffin-filled Drechsel bottle connected to the top of a condenser allowed the rate of evolution of ethylene to be monitored roughly. When all the dibromide had been added the mixture was refluxed for a further half hour. The heating mantle was removed and the condenser replaced by the transfer tube illustrated in Figure 2.7. Whilst the solution was still hot, it was transferred to another flask by nitrogen pressure. The porosity 2 filter stick removed any unreacted magnesium, the filtrate was colourless. The use of wide glass tubing (20mm o.d.) and an S29 ball-joint prevented blocking of the transfer tube by any magnesium bromide that happened to precipitate as a result of cooling.

Poly(α-methylstyryl) lithium and di-sodium α-methylstyryl tetramer were prepared as described in sections 2.3.3. and 2.3.4. and reacted with a 1M excess of anhydrous magnesium bromide solution

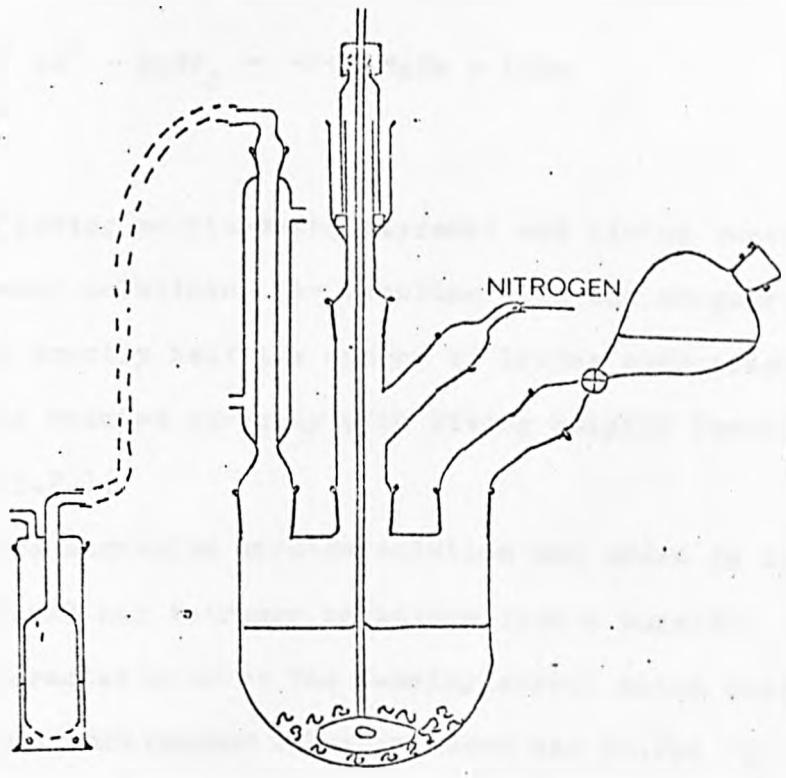


FIGURE 2.6. APPARATUS USED FOR THE PREPARATION OF MAGNESIUM BROMIDE SOLUTION.

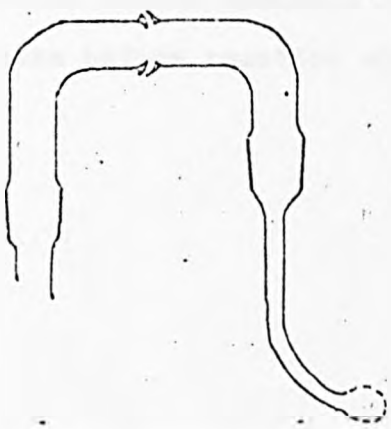


FIGURE 2.7. APPARATUS USED FOR TRANSFERRING MAGNESIUM BROMIDE SOLUTION TO ANOTHER FLASK.

in THF, which was calculated to terminate all the living ends in the manner shown in equation (2.3.).

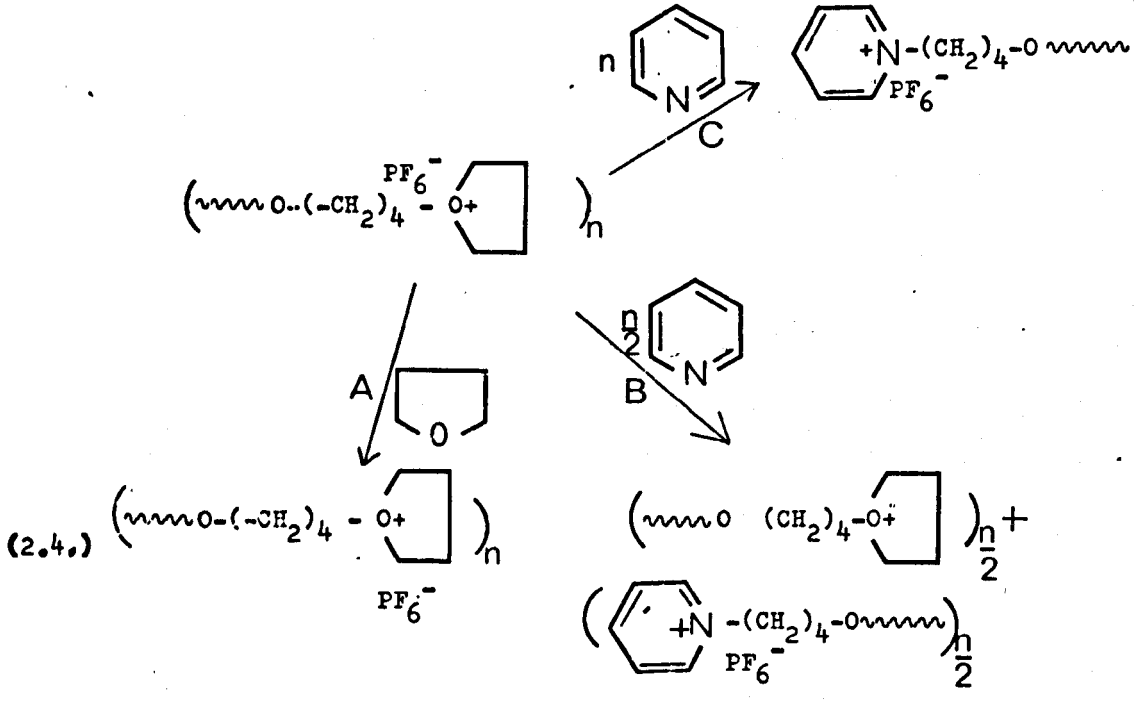
$$Na^+ \ ^-\alpha_4^- \ Na^+ + 2MgBr_2 \rightarrow BrMg- \ \alpha_4 \ -MgBr + 2NaBr$$

$$<><><> M^- \ Li^+ + MgBr_2 \rightarrow <><M-MgBr + LiBr \qquad (2.3.)$$

For both the living poly(α-methylstyrene) and living α-methylstyrene tetramer solutions, the reaction with the Grignard reagent accounted for exactly half the number of living ends present, the other half was reacted directly with living polyTHF (sections 2.5.1. and 2.5.2.).

The cooled magnesium bromide solution was added to the poly (α-methylstyrene) and tetramer solutions from a burette. The deep red colour characteristic of the α-methylstyryl anion disappeared when the volume of Grignard reagent solution added was 54.8ml for the poly (α-methylstyrene) (0.00817M) and 180.5ml for the tetramer solution.

A sample for g.p.c. analysis was always withdrawn from the living solutions before reaction with the Grignard reagent.


n
N
C
+N-(CH2)4-O
PF6-
PF6-
O+
n
A
O
n/2
N
B
(2.4.)
O-(-CH2)4 - O+
n
PF6-
O (CH2)4-O+
n/2 +
+N -(CH2)4-O
PF6-
n/2

2.4.3. Reaction of living polyTHF with pyridine

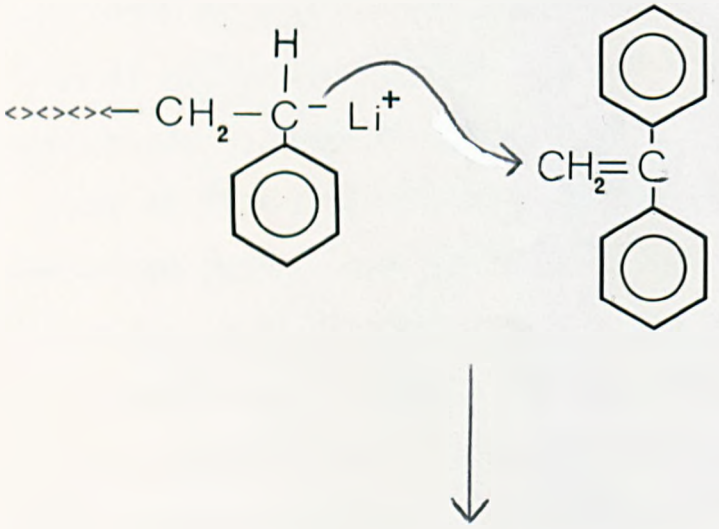
A 0.01M polyTHF solution (300ml) was prepared as outlined in section 2.3.5. and left to polymerise for one hour at 265K; then it was filtered (procedure given in section 2.3.5.) and divided into three equal volumes (100ml) A,B,C, by means of the burette. The three filtered living polyTHF solutions were left to polymerise further for two hours at 263K and then treated as follows: To A was added a further 5ml aliquot of THF, to B was added a 5ml THF solution containing half the stoichiometric volume of pyridine (0.04ml) required to terminate all the living polyTHF chains and to C a 5ml THF solution with the stoichiometric amount of pyridine (0.08ml) (equation (2.4.)).

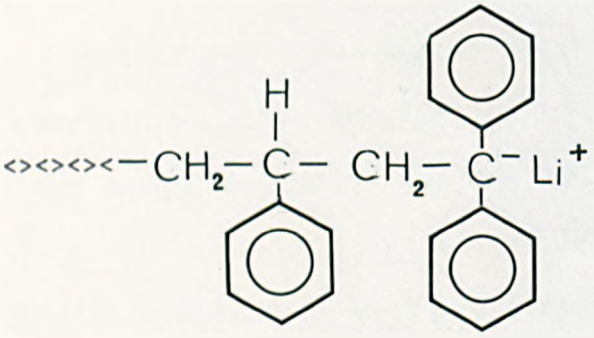
Because the volume of pyridine needed was small, a stock solution was made up in THF. For example, to 0.4ml of pyridine was titrated 24.6ml of THF, a 5ml portion of this solution was then added to the living polyTHF solution.

A 5ml aliquot was removed from solution A, injected into methanol and the polymeric sample obtained was used as a g.p.c. standard.

The polymerisation of the three portions A,B and C was continued for three hours at 263K. After this time samples of each were terminated with methanol, and the polymers were analysed by g.p.c.

A reaction was carried out in which samples of a 0.01M living polyTHF solution were terminated with pyridine as a function of time. The 0.01M polyTHF (100ml) was prepared as described in section 2.3.5. and left to polymerise for six hours at 263K, during which time 10ml samples were withdrawn and injected into





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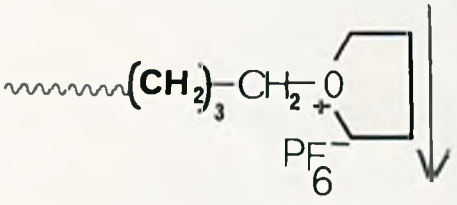


COPOLYMER?

excess (~10%) pyridine in THF (10ml) at 263K.

The reaction mixture was filtered after about 40 minutes, and the first 10ml sample (D) removed and injected into excess of pyridine. The unreacted pyridine and residual THF were evaporated off to leave the polymeric material. This procedure was repeated at different times up to six hours and the polymers analysed by g.p.c.. Discussion of the g.p.c. traces is given in Chapter 3 (section 3.2.5.) P.m.r. spectra were run on the first pyridine-polyTHF sample (D) and discussion of these is given in section 3.3.

2.4.4. Reaction of polystyryl lithium with 1,1-diphenylethylene

The aim of the preparation was to generate a sterically hindered anion which could be used to study the effect such an anion had on the coupling reaction with polyTHF cations (equation (2.5.)).

The experimental procedure used was necessary since 1,1-diphenylethylene does not homopolymerise; the large steric strain, caused by the presence of two bulky phenyl groups on every alternate carbon atom of the hypothetical homopolymer prevents normal head to tail polymerisation.

A 2.5 fold excess of 1,1-diphenylethylene over the number of polystyryl chains was required to achieve 100% "capping" of the living polystyrene ends. A polystyryl lithium of 15,000 M.W. was prepared as described in section 2.3.1. 1,1-Diphenylethylene (0.45ml, 0.46 moles) was added rapidly to a vigorously stirred living polystyrene solution. At the point of mixing a dark blue colour was observed, which diffused rapidly into the red solution. The formation of the blue colour indicates that capping of the polystyryl

chains by 1,1-diphenylethylene is not quantitative. Since benzophenone which is present as an impurity in the 1,1-diphenylethylene solution can react with the polystyryl anions to generate a blue coloured electron transfer complex.

Samples of the polystyryl lithium and the lithium 1,1-diphenylethylene-polystyrene polymer were withdrawn and isolated in methanol for g.p.c. analysis. The remainder of the 1,1-diphenylethylene-terminated polymer was made to react with a living polyTHF solution (95ml) as described in section 2.5.2. (i).

Only the theoretical titre of the anion solution was added to the living polyTHF solution, because in this system, unlike the polystyrene-polyTHF experiments, the red colour disappeared with the same rapidity at both the start of the titration and as the end point was approached.

2.5. Preparation of Block Copolymers

All the block copolymers were produced by the titration method (section 2.5.2.). The Grignard terminated anionic polymers gave no visible end point; in these systems only the calculated stoichiometric volume of the polymer solutions were added so as to avoid the presence in the isolated products of excess homopolymeric material which exhibits a U.V. signal. Such material would have invalidated attempts to quantify the block copolymer formation by enhancing the U.V. signal from the genuinely uncoupled polymer, and thus yielded a misleading signal intensity. This would have exaggerated the inefficiency of block copolymer formation compared with a competitive side reation. For the same reasons it was necessary to obtain a precise end point between the living anionic and living cationic polymers if meaningful g.p.c. analysis were to be performed and reproducible results obtained. The rate of addition of the anion solution to the living polyTHF can be a critical factor in maximizing the molecular weight, especially for the $(AB)_n$ block copolymer. Although no gelling was evident as had been reported previously[6], the rapid increase in polymer molecular weight which occurred as the equivalence point was approached resulted in a correspondingly rapid increase in the viscosity of the solution. Thus, even with powerful stirring it was difficult to avoid laminar flow completely and, despite the reaction between the component polymers being intrinsically very rapid, the titration had to be slowed down to allow sufficient time for red colour of the difunctional polystyryl solution to diffuse away before a further aliquot was added. Failure to control this would have resulted in an overshoot of the titre and consequently the molecular weight of the block copolymer would

TABLE 2.1.

THE BLOCK COPOLYMERS PREPARED

No. of Experiments	Cation (M.W.)	Anion (M.W.)	Copolymer (M.W.)
3	Monofunctional polyTHF (10,000)	Monofunctional polystyrene (20,000)	AB poly(styrene-b-THF (30,000)
2	Difunctional polyTHF (40,000)	Monofunctional polystyrene (10,000)	ABA poly(styrene-b-THF) (60,000)
2	Difunctional polyTHF (12,000)	Difunctional polystyrene (6,000)	$(AB)_n$ poly(styrene-b-THF) (200,000)
2	Monofunctional polyTHF (10,000)	Monofunctional poly(α-MS)(5,500) (a)	10,000 (b)
2	Monofunctional polyTHF (5,000)	Monofunctional poly(α-MS)(12,000)	12,000 (b)
2	Monofunctional polyTHF (5,000)	Monofunctional poly(α-MS)-MgBr (12,000)	12,000 (b)
4	Monofunctional polyTHF (5,500)	α-MS tetramer (α_4)	5,500 (b)
3	Monofunctional polyTHF (16,000)	MgBr α-MS tetramer-MgBr	16,000 (b)
1	Monofunctional polyTHF (37,000)	1,1-diphenylethylene-polystyrene (15,000)	(c)
1	Monofunctional polyTHF pyridine terminated (20,000)	α-MS tetramer	(c)

(a) poly α-MS is an abbreviation for poly(α-methylstyrene).

(b) This is not the M.W. of the copolymer, since the amount of block copolymer which was formed was not sufficient to cause a significant change in the homopolymer retention times on the g.p.c. instrument. The percentage block copolymerisation in these systems was measured by u.v. analysis.

(c) There appears to be no block copolymer formation.

Discussion of all the results is given in section 3.2.

have been controlled by this excess. A broadening of the low molecular weight tail of the copolymer g.p.c. trace would consequently have been observed.

2.5.1. Copolymer combinations

Table 2.1. lists the different copolymers which were prepared during this study.

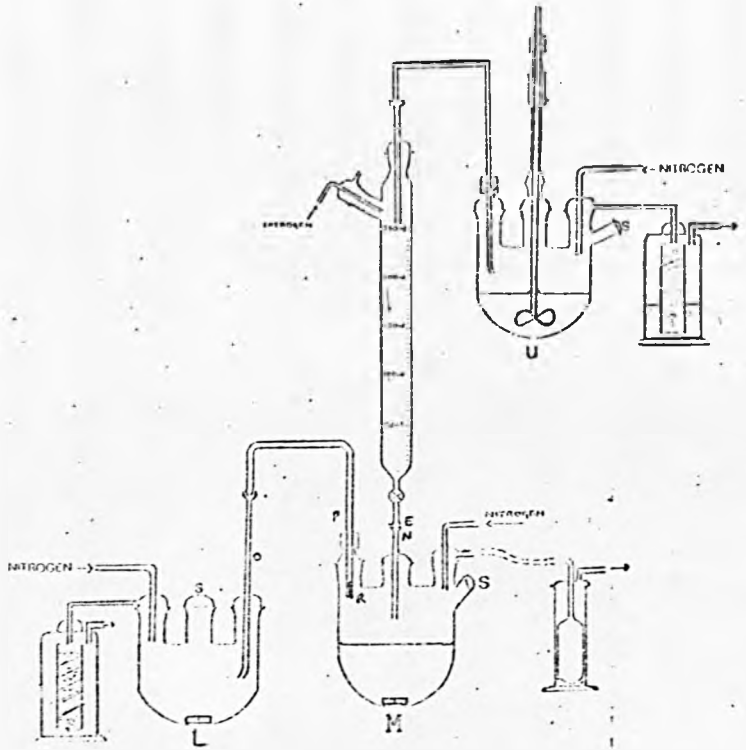
2.5.2. Titration technique

A titration method by which the formation of block copolymers would be controlled quantitatively was used throughout the work. This titration technique enabled stoichiometric addition of living homopolymers to be made accurately. A detailed account of this procedure is as follows: The apparatus used is shown in Figure 2.8. The 0.01M polyTHF solution was prepared as described in section 2.3.5. and was filtered through a sinter (R), the porosity of which was selected according to the molecular weight of the polyTHF; e.g. for molecular weights >10,000 a porosity 2 was always used. When this solution had been transferred into the flask M, a sample (10ml) was removed for g.p.c. analysis, and the temperature of the living polymer solution was adjusted to 253-243K. Transfer of the polyTHF depended on the viscosity of the mixture, and could take up to ten minutes.

2.5.2. (1) Reaction of polystyryl anions with polyTHF cations

The living polystyrene solutions (0.0036-0.018M) were prepared and carried into the burette (see Figure 2.8.) as described in section 2.3.1. Only after the polyTHF had been filtered and

FIGURE 2.8. APPARATUS FOR THE PREPARATION OF BLOCK COPOLYMERS



thermally stabilized was the polystyrene solution brought over into the burette. There was no innate difficulty in this exercise even when high molecular weight polystyrene solutions were used. The ball-joint E of the burette was connected to the socket N of the reaction flask M. The titration of the living polystyryl anion solutions into the living polyTHF was carefully executed since it was imperative not to add more than the stoichiometrically required volume if the analysis on the copolymeric product were to be meaningful. Thus, a dropwise addition of the anion solution into the polyTHF was always made from approximately 2ml before the theoretical end point. The achievement of the end point was taken as coinciding with the appearance of a permanent red tinge to the solution. The temperature of the polyTHF solution was always kept well below 263K throughout all the titrations performed. When both component polymers were difunctional, and hence a high molecular weight product was expected, a marked increase in the viscosity of the solutions occurred and powerful stirring had to be supplied to prevent laminar flow and to ensure complete mixing. The polymer samples withdrawn were isolated in methanol and then submitted for g.p.c. analysis.

A record of the different titre values and the various g.p.c. traces from the different reactions between these two species are shown in section 3.1., where a detailed consideration is given to their significance.

2.5.2. (2) Reaction of poly (α-methylstyryl) anions and Grignard terminated poly(α-methylstyrene) with polyTHF cations

Once prepared by the methods described in their respective sections 2.3.5. for the 0.01M polyTHF and 2.3.3. for the poly(α-methylstyrene), the procedure of transfer and the precautions followed are those mentioned in the preceding section (2.5.2. (1). However, the 0.0176M poly(α-methylstyrene) solution was titrated into the 0.01M living polyTHF solution (90ml) as soon as a 5ml sample was removed for g.p.c. analysis; it was not allowed to spend unnecessary time in the burette, because inevitable warming of the solution might have caused appreciable depropagation.

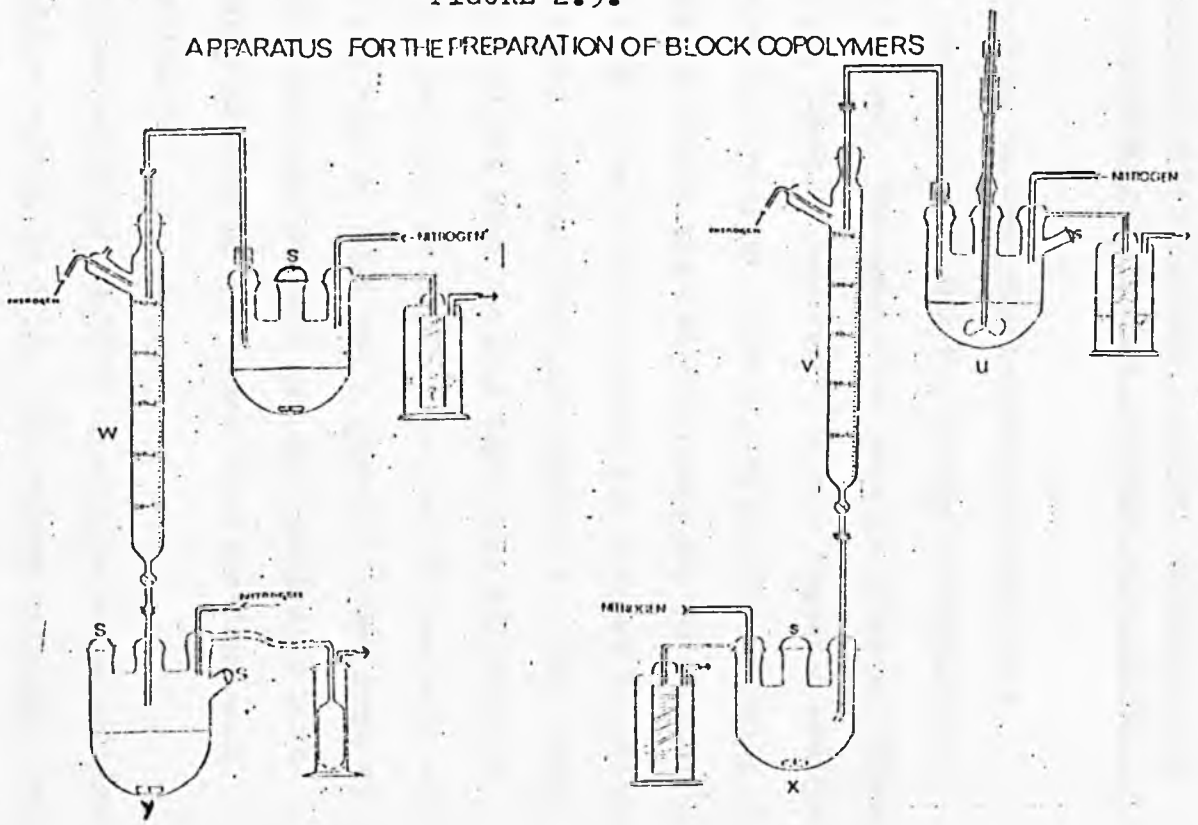
A series of experiments were performed in which a 0.01M living polyTHF solution (M.W. 5,000) was reacted with a higher molecular weight living poly(α-methylstyrene) solution (M.W. 12,000). These reactions are directly analogous to those involving polyTHF and polystyrene. A variation was attempted in a second set of experiments which involved dividing the 0.01M living polyTHF (100ml) solution into two (50ml) portions X and Y as described in section (2.3.5.) and these were then kept at 250K. A 5ml sample was removed from each portion for g.p.c. analysis before titration with the living 0.0082M poly(α-methylstyrene) solution.

Sufficient of the 0.0083M living poly(α-methylstyrene) solution (theoretical titre 54.2ml) to neutralise all the living 0.01M polyTHF solution (45ml) was transferred to the burette V in Figure 2.9., and titrated as described in section 2.5.2. (1) the actual titre was 55.9ml.

The colourless solution of poly(α-methylstyrene) magnesium bromide was carried into a burette and a slight excess over the theoretical titre was added (55.5ml) to the living polyTHF solution (45ml), Y (equation (2.3.)).

FIGURE 2.9.

APPARATUS FOR THE PREPARATION OF BLOCK COPOLYMERS



Polymer samples for g.p.c. analysis were removed before and after the titration. The g.p.c. traces and discussion of them is given in Chapter 3 (section 3.2.).

2.5.2. (3) Reaction of α-methylstyryl tetramer di-anions and the di-Grignard-terminated tetramer with polyTHF cations

In a manner similar to the poly(α-methylstyrene) work, reactions between living polyTHF and the living α-methylstyryl tetramer were carried out. The apparatus used is shown in Figure 2.9. but the reaction flask U was fitted with a magnetic stirrer instead of the mechanical stirrer. The 0.01M polyTHF solution (500ml) was prepared at 263K, and left to react for 45 minutes before cooling to 195K. The silver bromide was removed by filtration through a porosity 3 sinter into the burette W. The clear living polyTHF solution was then divided into five aliquots of 100ml each. One (A) was kept at 195K, a second (B) was kept at 223K, a third (C) was kept at 253K and a fourth (D) was kept at 263K; the fifth (E), was held at 195K but was terminated with methanol before the titration of the other four portions with living tetramer solution.

A living tetramer solution (0.167M) was prepared as outlined in section 2.3.4. and was cooled to 195K. The volume required (6ml) to react with one of the portions of the polyTHF solution was transferred to the burette (W). The titration was carried out as quickly as possible to minimize any deviation from the temperature of the coolant baths (195K). The living tetramer solution was warmed to 223K

and the procedure was repeated; likewise for 253K and 263K. The titre values are given in Table 3.1.1.(Chapter 3).

At a later date, a re-run of the experiment was carried out in which only 50% of the required living tetramer solution was added to the living polyTHF solutions.

A duplicate experiment was performed in which the stoichiometric volume of the Grignard-terminated α-methylstyrene tetramer was added to the polyTHF solutions. The Grignard-terminated tetramer was prepared as described below. A solution of magnesium bromide in THF (0.33M) was prepared (section 2.4.2.) and added to a living tetramer solution (0.167M) The red colour disappeared after addition of 180.5 mls (the remaining volume was added rapidly).

The colourless solution was cooled to 195K. A polymerisation of THF for which silver hexafluoroantimonate (1.376g, 4.0mmole) had been used as the initiator, was left to polymerise for three hours at 263K, before filtration into the burette W shown in Figure 2.9. The 0.01M living polyTHF solution (400ml) was divided into four 100ml portions, the first (A) was cooled to 195K, the second (B) was kept at 253K and the third (C) held at 263K and the fourth (D) kept at 195K but was terminated with methanol before the titration of the other three samples.

The Grignard-terminated tetramer was transferred quickly into the burette and its theoretical volume (6ml) was added to solution (A) at 195K. The excess Grignard-tetramer reagent was discarded and the procedure was repeated with solutions (B) and (C) at 253K and 263K.

G.p.c. data for all the polyTHF-tetramer experiments are reviewed in Chapter 3 (section (3.2.)).

2.5.2. (4) Reaction of 1,1-diphenylethylene anions with polyTHF cations

The method for the synthesis of the 1,1-diphenylethylene-terminated polystyrene has been given in section 2.4.5. (equation (2.4.)), the apparatus used for its reaction with living polyTHF is shown in Figure 2.8. The 0.0055M anionic solution was carried into the burette, by nitrogen pressure, a 5ml sample was removed for g.p.c. analysis before titrating into the 0.01M polyTHF (90ml) solution until the theoretical titre of 169.8ml was reached. However, no clearly visible end-point was observed as in the other experiments (see Section 2.4.5.). Samples of the homopolymers and of the copolymer solutions were analysed by g.p.c.

2.5.2. (5) Reaction of α-methylstyryl tetramer di-anions with pyridine-terminated polyTHF

A 0.167M solution of α-methylstyryl tetramer (163ml) was prepared as described in section 2.3.4. A previously prepared polystyrene (140,000 M.W.) was vacuum dried and 2g of it was added to the reaction flask (U) (Figure 2.8.). The purpose of the polystyrene was to provide a U.V. reference; this point is explained in detail in section 3.2.6.

A 0.01M living polyTHF solution (100ml) was prepared (section 2.3.5.) and filtered into a flask M, after a three and a half hour reaction at 263K, a sample of the clear solution was removed and isolated from methanol to act as a standard for g.p.c. analysis. A pyridine (0.08ml) in THF (5ml) solution was added to the polyTHF solution. The tetramer solution (20ml) was forced into the burette and connected to the flask (M) containing the pyridine terminated 0.01M polyTHF solution (90ml) (Figure 2.8.). On addition of

approximately one third (2ml) of the theoretical amount (5.4ml) the reaction mixture turned deep red, this colour changed to brown on addition of the stoichiometrically required volume of tetramer solution. A sample was removed and injected into methanol (in which it retained the red colour), isolated and submitted for g.p.c. analysis. The g.p.c. traces obtained and their interpretation are given in Chapter 3 (section 3.2.6.).

2.6. Isolation Procedures

2.6.1. PolyTHF

If the g.p.c. instrument was available then the polyTHF-methanol solution was placed on a rotary evaporator to remove the solvents (i.e. THF and methanol) and leave only the polyTHF. A sample (10mg) of this polymer was dissolved in 10ml of THF, filtered and injected into the g.p.c. instrument.

When the instrument was occupied by other users, the polyTHF-methanol solution was reduced in volume to approximately half by rotary evaporation before a series of brine-ether extractions were carried out. The ethereal fraction was dried with anhydrous magnesium sulphate, and evaporated to dryness to prepare the standard from it.

The pyridine terminated polyTHF samples were isolated by the first procedure only.

2.6.2. Polystyrenes and polyα-methylstyrenes

Samples of the homopolymer were injected into methanol. The solid white powdery product was filtered, dried in a vacuum oven and made up to a 0.1% w/v. THF solution as for the polyTHF (section 2.6.1.).

The 1,1-diphenylethylene terminated polystyrene was also isolated by this method.

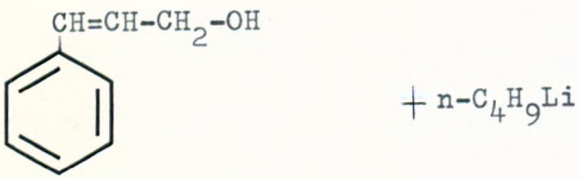
2.6.3. α-Methylstyrene tetramer

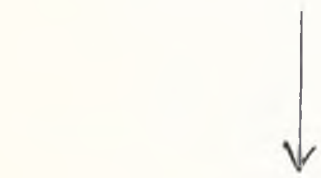
Because of its low molecular weight (474), the α-methylstyrene tetramer is soluble in methanol. Therefore the tetramer-methanol solution was evaporated to obtain the tetramer. 10mg of this was analysed by g.p.c., and g.l.c. analysis was also undertaken as described in section 2.3.4.

2.6.4. Block copolymers

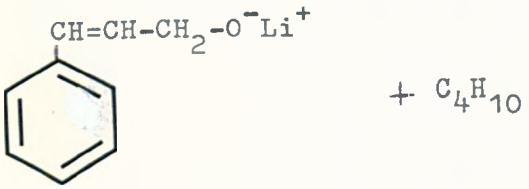
With the exception of the block copolymers composed of α-methylstyrene tetramer and polyTHF, all the copolymeric products were precipitated in methanol, filtered, and dried in a vacuum oven before being prepared for g.p.c. analysis.

Those of the α-methylstyrene tetramer-polyTHF were isolated by rotary evaporation of the methanol solution to dryness and the last traces of solvent were removed by use of a vacuum pump.

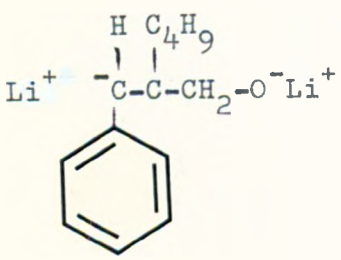




(2.6.)



YELLOW



RED

2.7. Cationic to Anionic Transformation

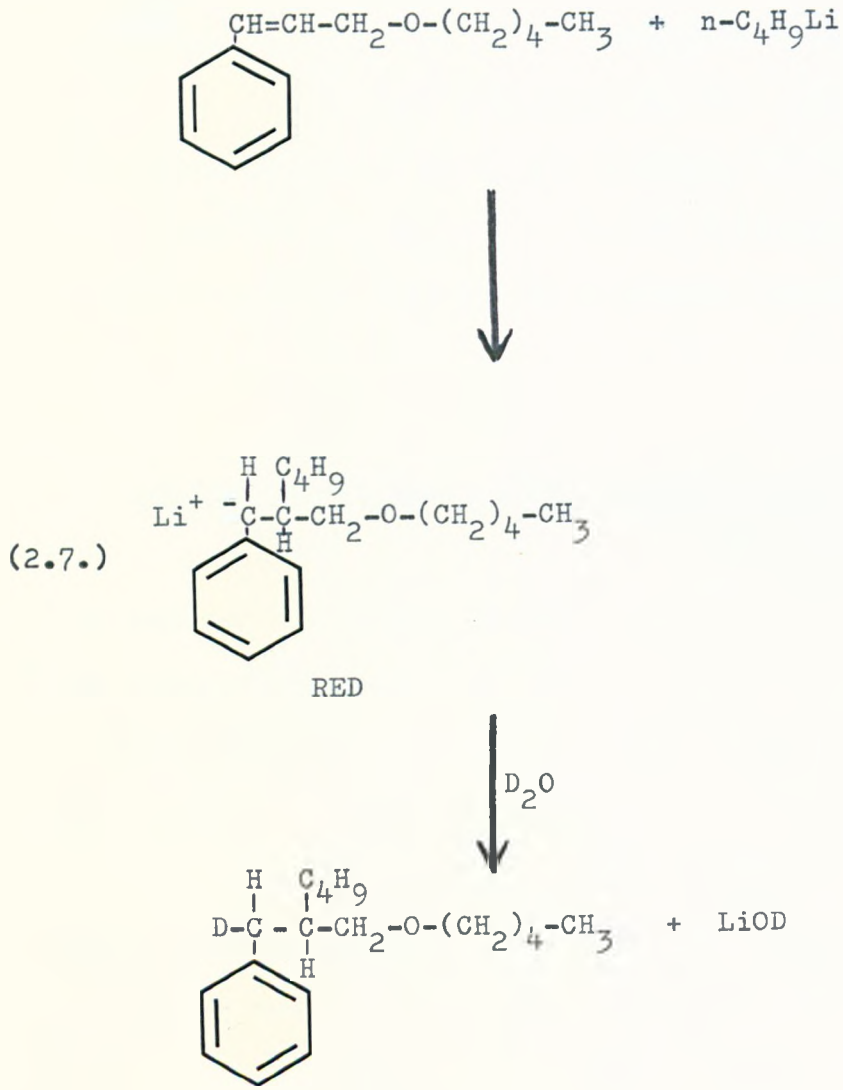
2.7.1. Preparation of cinnamyl alkoxide

1.6.M n-Butyl lithium solution (1.5ml, 2.4 mmole) was added dropwise, under nitrogen, to a stirred solution of cinnamyl alcohol (0.33g, 2.5mmole) in benzene (70ml)/THF (2ml). A pale orange colouration which is thought to be indicative of alkoxide formation was obtained. The addition of a further aliquot (0.5ml) of butyl lithium produced a red colour which is characteristic of the benzylic anion (equation (2.6.)). This colour was observed in subsequent experiments described in sections 2.7.4., 2.7.5. and 2.7.8.

2.7.2. Preparation of the cinnamyl amyl ether [(3-phenylprop-2-enyloxy) pentane]

Cinnamyl alkoxide (0.025 mole) was prepared as described in section 2.7.1., n-pentyl bromide (3.0ml, 0.025 mole) was added and the mixture refluxed for one hour. The precipitate formed was filtered before the solvents (THF (10ml) and benzene (250ml)) were evaporated from the filtrate to leave an oily residue.

The ether was obtained pure, free from alcohol, after passage of the oil through a silica column. The purity of the ether was found by g.l.c. and p.m.r. to be >95%.


CH=CH-CH2-O-(CH2)4-CH3 + n-C4H9Li
Li+ -C-C-CH2-O-(CH2)4-CH3
H C4H9
H
RED
D2O
D-C - C-CH2-O-(CH2)4-CH3 + LiOD
H C4H9
H

(2.7.)

2.7.3. Preparation of [(4-phenylbut-3-enyloxy)pentane]

The alcohol 4-phenylbut-3-en-1-ol was prepared by Lewis' method[72] and used to synthesize the ether by the procedure described in section 2.7.2.

The purity of the ether was found by g.l.c. and p.m.r. to be >95%.

2.7.4. Reaction of n-butyl lithium with cinnamyl amyl ether [(3-phenylprop-2-enyloxy) pentane]

This reaction was carried out in three different solvent systems: (1) THF, (2) benzene and (3) THF-benzene (1:2). A general method is outlined below in which the solvent used was THF.

Cinnamyl amyl ether (2.04g, 0.01 mole) was dissolved under nitrogen, in THF (50ml) at 263K and butyl lithium (5.0ml, 0.01 mole) was added slowly by syringe. A red colour was formed, (equation (2.7.)). The mixture was reacted for up to 3 hours, samples were withdrawn by syringe, injected into deuterium oxide, and submitted for p.m.r. analysis. The experimental results of this reaction and those of the reactions described in sections 2.7.5, 2.7.7. and 2.7.8. are discussed in section 3.5.

2.7.5. Reaction of n-butyl lithium with [(4-phenylbut-3-enyloxy) pentane]

The experiments were carried out in an identical manner to those reported in section 2.7.4. A postulated mechanism for the reaction between butyl lithium and (4-phenylbut-3-enyloxy)pentane is shown in equation (2.7.).

2.7.6. Preparation of benzyl butyl ether

n-Butyl lithium (5ml, 0.01 moles) was added slowly by syringe to a stirred mixture of butanol (0.5, 0.01 mole) in THF (30ml), under nitrogen at 298K. Benzyl bromide (0.12ml, 0.01 mole) was then added to the reaction mixture. Evaporation of about half the volume of solvent caused precipitation to occur. The precipitate was filtered before the remaining solvent was evaporated to yield the ether as a yellow liquid. The purity of ether was found by g.l.c. to be >95%.

2.7.7. Reaction of benzyl butyl ether with n-butyl lithium

Benzyl butyl ether (1.62g, 0.01 mole) prepared as described in section 2.7.6. was dissolved in THF (30ml) under nitrogen, and the stirred solution cooled to 263K. n-Butyl lithium (5ml, 0.01 mole) was added slowly by syringe to the ether solution, no colour was formed (equation (1.2.6.)). The reaction mixture was kept at 263K for 3 hours during which time samples were removed and analysed by g.l.c.

A similar reaction was carried out using benzene at 273K, and the reaction mixture analysed by g.l.c.

2.7.8. Reaction of equimolar quantities of benzyl butyl ether and cinnamylamyl ether in benzene with n-butyl lithium

Benzyl butyl ether (1.62g, 0.01 mole) and cinnamyl amyl ether (2.04g, 0.01 mole) were dissolved in benzene (30ml), under nitrogen, and the solution cooled to 273K. n-Butyl lithium (5.0ml, 0.01 mole) was added by syringe to the stirred solution, a red colour was formed. The mixture was reacted for 3 hours and samples removed for g.l.c. analysis.

2.8. Analytical Techniques

2.8.1. Gel permeation chromatography (g.p.c.)

Gel permeation chromatography is a modern versatile form of elution chromatography by which the molecular weight and dispersity of polymeric and oligomeric material can be determined. The technique was used in this work to identify and subsequently to measure the amount of block copolymer formation. It served also to record the presence of any component that possesses a U.V. absorption, for example, pyridine at the end of a polyTHF chain.

The polymer is dissolved in a carrier solvent and passed through a series of columns which are packed with an inert porous material; for the work reported in this thesis, columns of a cross-linked polystyrene gel of controlled porosity were used. Individual molecules are fractionated simply as a function of their size. Because the high molecular weight molecules are able to enter only the largest pores in the packing, they are eluted first as they take the shortest path through the columns. The smaller molecules which can diffuse into the pores more easily, are eluted later. The presence of polymer in the eluent may be detected by a differential refractive index, ultra-violet or infra-red detector. The response of the detectors is usually measured on a strip chart recorder.

The number average ($\bar{M}n$) and weight average ($\bar{M}w$) molecular weights are calculated from the shape of the distribution curve provided that the set of g.p.c. columns has been calibrated with monodisperse standard polymers. The variation of molecular weight

with elution volume is logarithmic and a typical calibration curve AB is shown in Figure 2.10. V_o is the point of sample injection. V_1 is the "excluded volume" and corresponds to the interstitial volume of solvent in the columns and hence the time taken for totally excluded molecules to be eluted. V_2 corresponds to the time taken for even the smallest molecules to be eluted. The calibration is generally linear over most of the range V_1 to V_2 but deviates as these limits are approached, as shown in the Figure 2.10. The gradient of AB and the extrapolation of the ordinate to the intercept position, C, are a function of the "pore size" in the column packing material. The resolution of a particular polymer will depend on judicious choice of a combination of columns packed with material of different pore sizes which cover the range of molecular weight in the sample.

A typical g.p.c. trace is shown in Figure 2.11. The molecular weight M_i at elution volume V_i may be found from the calibration curve for the column set. The response H_i of the differential refractometer detector at elution volume V_i is proportional to the mass of polymer per unit volume of molecular weight M_i. If n_i is the number of molecules per unit volume of molecular weight M_i, then $H_i \propto n_i M_i$.

$\bar{M}n$ and $\bar{M}w$ are defined as

$$\bar{M}n = \frac{\sum_{i=1}^{i=\alpha} n_i M_i}{\sum_{i=1}^{i=\alpha} n_i} \qquad \bar{M}w = \frac{\sum_{i=1}^{i=\alpha} n_i M_i^2}{\sum_{i=1}^{i=\alpha} n_i M_i}$$

and from $H_i \propto n_i M_i$, $\bar{M}n$ and $\bar{M}w$ can be expressed as follows,

$$\bar{M}n = \frac{\sum_{i=1}^{i=\alpha} H_i}{\sum_{i=1}^{i=\alpha} H_i/M_i} \qquad \bar{M}w = \frac{\sum_{i=1}^{i=\alpha} H_i M_i}{\sum_{i=1}^{i=\alpha} H_i}$$

The dispersity of the polymer is given by the ratio $\bar{M}w/\bar{M}n$.

FIGURE 2.10. Gpc. CALIBRATION CURVE.

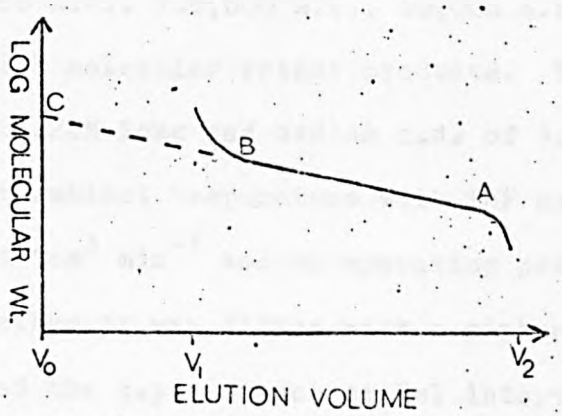
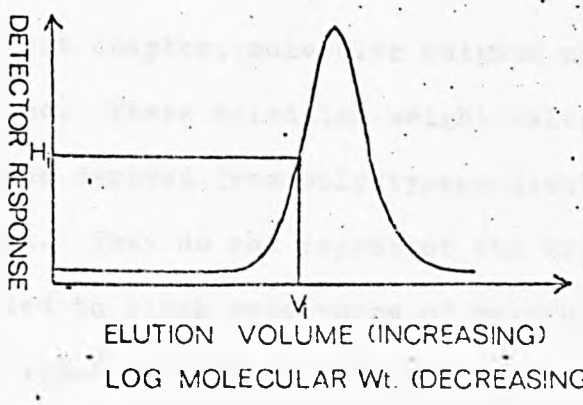


FIGURE 2.11. TYPICAL GEL PERMEATION CHROMATOGRAM



Gel permeation chromatography was carried out on a Waters Associates Model ALC/GPC 301 chromatograph fitted with a Waters differential refractomer thermostatted at 298K and a Waters fixed wavelength ultra-violet (254nm) detector. Two Styragel columns in sequence with porosities of 10,000 Ångström units (A.U.) and 1,000 A.U. were used for simplicity to monitor the medium and low molecular weight products, although a four column set with porosities 1,000,000 A.U., 100,000 A.U., 10,000 A.U. and 1,000 A.U. was used for the high molecular weight products. The columns were approximately 1.22M long and had an o.d. of 9.5mm. Elutions were carried out at ambient temperature with THF as solvent and with a flow rate of $1cm^3\ min^{-1}$ and an operating pressure of $0.84MNm^{-2}$. The instrument was fitted with a siphon which automatically calibrated the g.p.c. trace at 5ml intervals by the actuation of an event marker. To obviate the need to designate the particular column set used in each of the many g.p.c. traces reproduced in the next chapter, molecular weights at the peak maxima only are cited. These molecular weight values are based on calibration curves derived from polystyrene standards supplied by Waters Associates. They do not represent the true molecular weights when applied to block copolymers of polyTHF and other polymers. A 2ml aliquot of 0.1% w/v THF solution of the products was injected.

2.8.2. Proton magnetic resonance (p.m.r.) spectroscopy

P.m.r. spectroscopy was used principally for the structural analysis of the polyTHF-pyridine adducts and the products of the cationic to anionic transformations. All the p.m.r. spectra were recorded on the J.E.O.L. PS-100MHz spectrometer,and used approximately 10% solutions in deuterochloroform with tetramethylsilane as the internal standard.

2.8.3. Gas-liquid chromatography (g.l.c.)

G.l.c. was used to ascertain the purity of the α-methylstyrene tetramer prepared, and in the exploratory investigation to assess the amount of block copolymer formation which occurred between living polyTHF and living α-methylstyrene tetramer. The difference in the areas of the g.l.c. traces obtained for α-methylstyrene tetramer before and after the copolymer reaction, is a measure of its percentage incorporation in the block-copolymer. A constant weight (10mg) of each material was dissolved in THF (20ml) and 3μl injected. However, this analytical technique was used only to confirm g.p.c. analysis,and so was abandoned after the preliminary study.

A Pye Unicam Series 104 dual column chromatograph with flame ionisation detectors was fitted with 2m glass columns of 4mm i.d. for analytical separations. The columns were packed with 1% OV 101on 80/100 mesh "Chromosorb G". In this system the mixtures were separated according to their boiling points.

References to CHAPTER 2.

65. H. Gilman and A.H. Haubein, J. Amer. Chem. Soc., 1944, 66, 1515.

66. T. Altares, D.P. Wyman and V.R. Allen, J. Polym. Sci. (A-2), 1964, 4553.

67. C.L. Lee, J. Smid and M. Szwarc, J. Phys. Chem., 1962, 66, 904.

68. A. Davis, D.H. Richards and N.F. Scilly, Makromol. Chem., 1972, 152, 121.

69. D.H. Richards and R.L. Williams, J. Polym. Sci., 1973, 11, 89.

70. D.E. Pearson, D. Cowan and J.D. Becker, J. Org. Chem. 1959, 24, 504.

71. M. Tissier and V. Grignard, Compt. Rend., 1901, 132, 835.

72. K.L. Lewis and J.D. Roberts, J. Amer. Chem. Soc., 1965, 87, 1331.

CHAPTER 3

RESULTS AND DISCUSSION

3.1. Preparation Results

The theoretical volume of anion solution to react stoichiometrically with the living polyTHF solution was calculated before any titration was performed. The calculation was approximate since (i) it assumed the concentration of living ends to be equal to that of the initiator, and (ii) it allowed for no volume reduction in the monomer solution either by polymerisation or by inadvertent loss. The latter source of error was observed in an early experiment during which too rapid a nitrogen flow was applied to the purified THF, which caused vaporisation of the liquid and so reduced quite considerably the volume in the reaction vessel. Repetition of the experiment under much reduced nitrogen flow, however, resulted in no appreciable loss of solvent and the expected titre was obtained, (see Tables 3.1. and 3.1.1. for the titres recorded during this study).

The efficiencies of block copolymer formation in the reactions studied were determined by the use of a dual detector g.p.c. only. The technique is of particular value when, as in this work, one of the component polymers, polyTHF, is transparent at the U.V. detector wavelength of 254nm and the other, e.g. polystyrene, absorbs strongly. In these systems block copolymer formation can be quantified not only by comparison of the product molecular weight and its distributions with those of the terminated constituent homopolymers, but also by a similar comparison of the relative responses of the U.V. and differential refractometer (D.R.) detectors. The latter technique has been applied previously to an examination of the efficiencies of anionic to cationic transformation reactions[73], and is outlined overleaf.

TABLE 3.1.

TITRE VALUES FOR THE REACTIONS OF THE LIVING POLYMERIC SPECIES

Experiment Number	Copolymer System	Titre ml. Theoretical	Titre ml. Actual	Efficiency (%)
SK 32 Series	AB poly(styrene-b-THF)	243.24	248.6	>95
SK 33 Series	ABA poly(styrene-b-THF)	257.2	264.1	>95
SK 34 Series	$(AB)_n$ poly(styrene-b-THF)	51.0	52.2	>95
SK 35 Series	AB poly(α-methylstyrene-b-THF)	51.1	52.4	∿20
	AB poly(α-methylstyrene-b-THF)	54.2	55.9	∿20
SK 36 Series	AB poly(α-methylstyrene-MgBr-b-THF	54.2	55.0	∿20
SK 39 Series	AB (1,1-D.P.E.-polystyrene-b-THF)	163.6	164.0	NIL

TABLE 3.1.1.

TITRE VALUES FOR REACTION OF THE DI-GRIGNARD TERMINATED α-METHYLSTYRENE TETRAMER WITH LIVING POLYTHF AT VARIOUS TEMPERATURES[SK 36]

Temperature (K)	$\alpha_4^=$ Addition (ml)	
	Theoretical	Actual
263	6.0	6.1
253	6.0	6.0
195	6.0	6.1

a = area of U.V. signal for polystyrene (PS)

b = area of D.R. signal for PS

s = a/b = relative response factor for PS

r = relative response factor of the D.R. detector to polyTHF compared with polystyrene. r Is equal to the ratio of the D.R. areas of the two homopolymers at the same concentration.

c = area of U.V. signal for copolymer

d = area of D.R. signal for copolymer

Contribution from PS to the D.R. area of the copolymer = c(b/a)

Contribution from polyTHF to the D.R. area of the copolymer = d-c(b/a)

$$\text{Hence, } \frac{\text{weight of polyTHF in copolymer}}{\text{weight of PS in copolymer}} = \frac{d-c(b/a)}{c(b/a)} r = A$$

The value of A may be compared with that predicted from the observed molecular weights and functionalities of the component polymers; a conversion factor[73] (0.592) was used to obtain the actual molecular weight of polyTHF from its g.p.c. polystyrene equivalent.

A typical calculation is given below: Monofunctional PS of 7,000 M.W. with di-functional polyTHF of 40,000 M.W., was reacted to yield an ABA copolymer (g.p.c. trace 3.3.1.)

$$s = a/b = 10.37/8.79$$

$$c(b/a) = 7.2 \times 0.8475 = \underline{6.102}$$

$$d-c(b/a) = 9.37 - 6.102 = \underline{3.268}$$

$$A = \frac{3.268}{6.102} \times 2.99 = \underline{\underline{1.61}}$$

$$\frac{\text{Weight of polyTHF in copolymer}}{\text{Weight of PS in copolymer}} = \frac{\text{Actual M.W. of polyTHF}}{2(\text{M.W. of PS})}$$

$$= \frac{4 \times 10^5 \times 0.592}{1.4 \times 10^5}$$

$$= \underline{1.69}$$

Therefore, approximately 96% block copolymerisation has occurred.

Estimation and identification of the errors present in this method of analysis are outlined in Table 3.2.

TABLE 3.2.

ESTIMATION AND SOURCE OF ERRORS

SOURCE	ESTIMATE
The area measurement of the g.p.c. curve was carried out three times with a planimeter, before the average value was used in the calculation (section 3.1).	±2% error on an area of 10 cm^2
The assignment of the start and end of the g.p.c. curve, and the decision where the base-line of the curve should be drawn were standardised, by drawing a horizontal line as a continuation of the instrument's base-line.	±2-3% error

These errors were assessed by the method given in the appendix of Chapter 8.

3.2. Discussion of Results

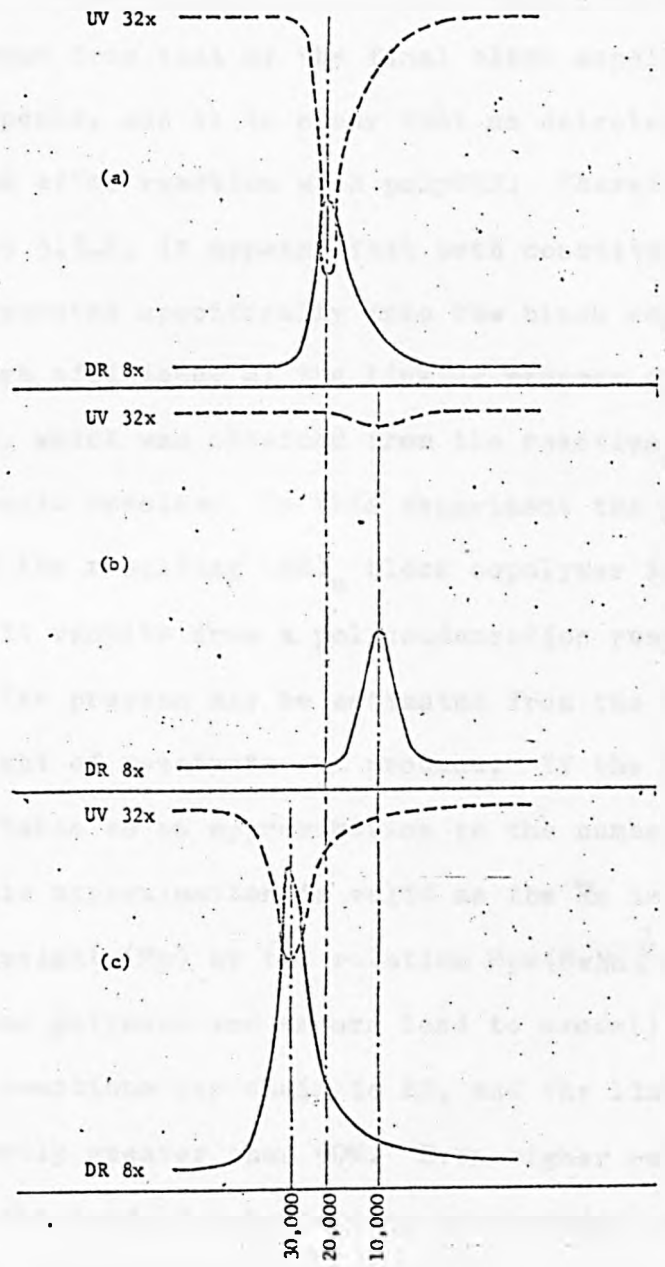
3.2.1. Living polystyrene and living polyTHF

Three series of experiments were carried out to examine the efficiency of the linking reaction between polystyryl anions and polyTHF cations (equation(1.1.)).The molecular weights of the component homopolymers were chosen to be as low as was consistent with obtaining a significant change in their retention times on the g.p.c. instrument.

From studying the g.p.c. traces (Figures 3.3.1.-3.3.3.) of the different products together with those of their methanol terminated homopolymer constituents certain observations are evident. The U.V. absorption of the homopolyTHF sample is always small but significant. This absorption is due to the initiators, benzyl bromide for monofunctional and p-xylylene dibromide for difunctional polymers, which become initial or central groups in the polymers[7]. No allowance for this small absorbance was made in the calculation of block copolymer formation.

In Figure 3.3.1. the molecular weight of product has a higher value than that of the component polymers and it exhibits significant absorption in the U.V., which indicates the presence of a polystyrene segment which can only have resulted from the formation of AB block copolymer. The low intensity of the D.R. signal recorded for the copolymer at 10,000 M.W. indicates that little if any of the polyTHF remained unreacted. However, it is difficult to assess with certainty the efficiency of the polystyrene coupling, as residual uncoupled material at 20,000 M.W. may be buried under the copolymer envelope.

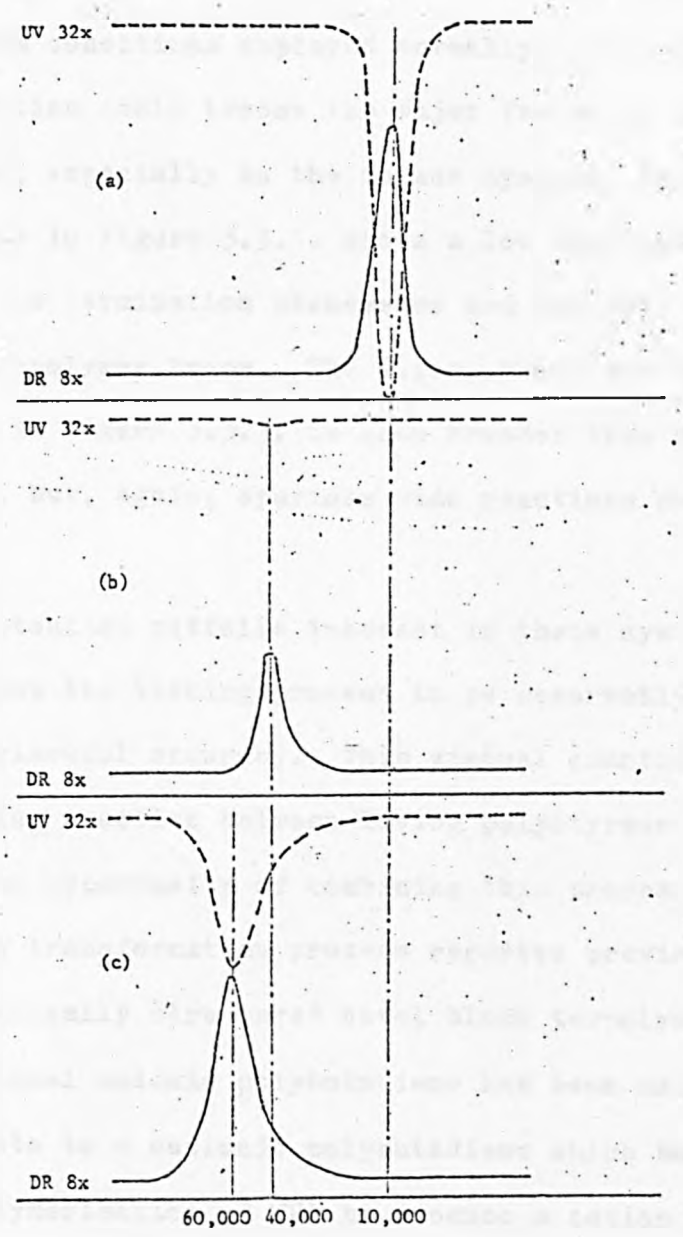
FIGURE 3.3.1.



Gpc traces of (a) protonated monofunctional polystyrene, (b) methoxy-terminated monofunctional polyTHF, and (c) the product of the reaction between these two living polymers.

Analysis of Figure 3.3.2. which shows the g.p.c. traces of reactants and product for the reaction to form ABA poly(styrene-b-THF), indicates that the coupling efficiency of living polystyrene is very high. The retention time of the polystyrene standard is sufficiently different from that of the final block copolymer to avoid any overlapping peaks, and it is clear that no detectable homopolystyrene remains after reaction with polyTHF. Therefore, from Figures 3.3.1. and 3.3.2. it appears that both constituent homopolymers are incorporated specifically into the block copolymer. Confirmation of the high efficiency of the linking process can be seen from Figure 3.3.3. which was obtained from the reaction of the two difunctional polymeric species. In this experiment the molecular weight distribution of the resulting $(AB)_n$ block copolymer is understandably broad since it results from a polycondensation reaction, but the efficiency of the process may be estimated from the dramatic shift in molecular weight of reactants and product. If the peak molecular weights are taken as an approximation to the number average molecular weights, (this approximation is valid as the $\bar{M}n$ is related to the peak molecular weight (Mp) by the relation $Mp=(MwMn)^{\frac{1}{2}}$ and so $\bar{M}n$ is less for all three polymers and errors tend to cancel) then the number of linking reactions per chain is 22, and the linking efficiency is consequently greater than 90%. Even higher estimates of the efficiency are obtained if calculations are carried out based on the residual differential refractometer signals at 12,000 and 6,000 M.W. A value greater than 95% was obtained for the difunctional polyTHF/monofunctional polystyrene system by the analysis described in section 3.1. which involved a comparison of the U.V. and differential refractometer signals.

FIGURE 3.3.2.

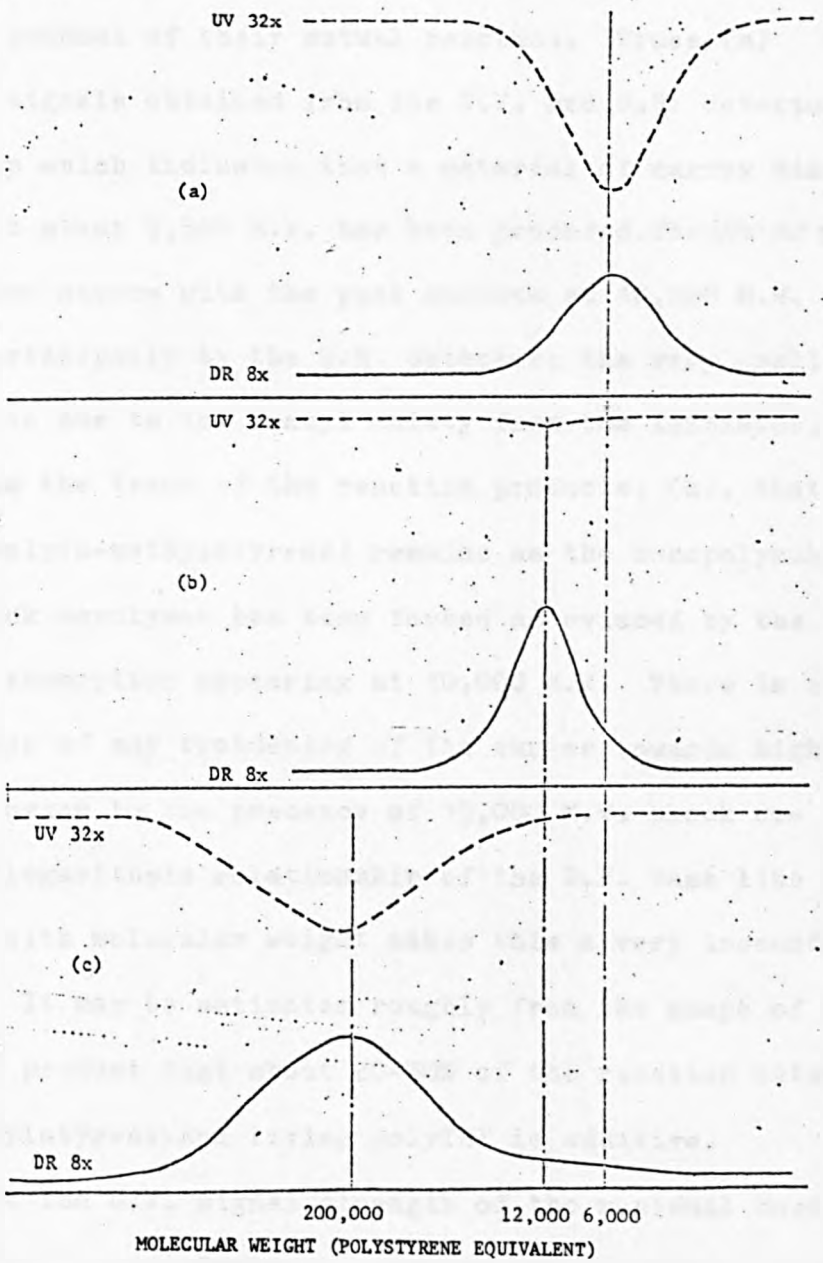


Gpc traces of (a) protonated monofunctional polystyrene, (b) methoxy-terminated difunctional polyTHF, and (c) the product of the reaction between these two living polymers.

There are factors which can reduce the efficiency of the linking process. These include inadvertent termination of the living polymers by adventitious impurities for polystyrene or by a small amount of chain transfer for polyTHF, and, because these materials were prepared under nitrogen rather than under the more rigorous high vacuum conditions employed normally, it is very likely that termination could become the major factor to limit block copolymer formation, especially in the former system. The g.p.c. trace of polystyrene in Figure 3.3.1. shows a low M.W. tail which is characteristic of the termination phenomenon and the tail is also seen in the block copolymer trace. The g.p.c. trace for the difunctional polystyrene in Figure 3.3.3. is also broader than expected for living polymer, but, again, spurious side reactions could account for this.

Despite the potential pitfalls inherent in these systems, the g.p.c. traces do show the linking process to be remarkably quantitative within experimental accuracy. This virtual quantitative nature of the linking reaction between living polystyrene and living polyTHF opens up the opportunity of combining this process with the anionic to cationic transformation process reported previously[10,73,74]. to synthesize specifically structured novel block terpolymers. For example, monofunctional anionic polybutadiene has been oxidised via a stable intermediate to a cationic polybutadiene which has initiated efficiently the polymerisation of THF to produce a cationic AB block copolymer[74]. Titration of living polybutadiene solution with monofunctional living polystyrene would yield uniquely an ABC poly(butadiene-b-THF-c-styrene) terpolymer that should possess interesting morphological properties.

FIGURE 3.3.3.



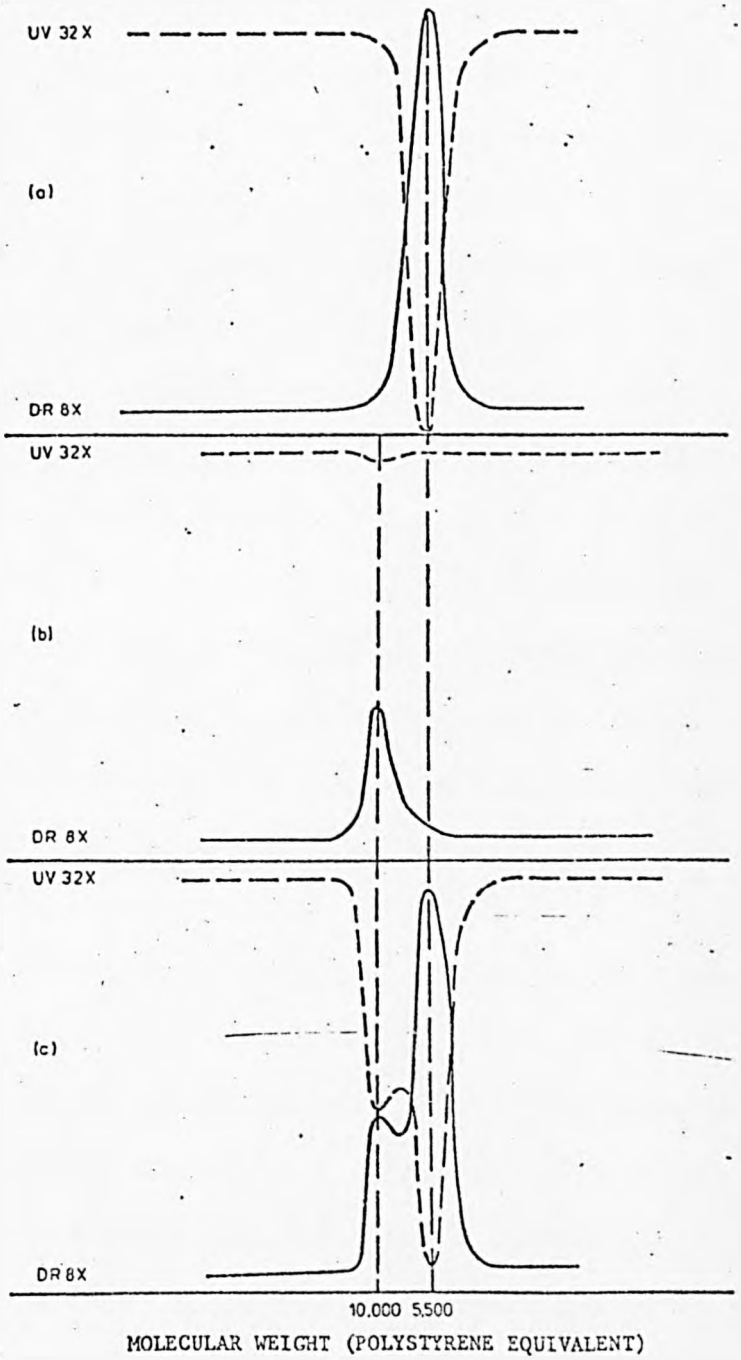
Gpc traces of (a) protonated difunctional polystyrene, (b) methoxy-terminated difunctional polyTHF and (c) the product of the reaction between these two living polymers.

3.2.2. Living poly(α-methylstyrene) and living polyTHF

Results of the experiments involving monofunctional living poly(α-methylstyrene) and monofunctional living polyTHF are shown as g.p.c. traces in Figures 3.3.4. and 3.3.5. Figure 3.3.4. compares the g.p.c. traces of the two methanol-terminated homopolymers with that of the product of their mutual reaction. Trace (a) shows the strong signals obtained from the U.V. and D.R. detectors; the trace is sharp which indicates that a material of narrow dispersity centred at about 5,500 M.W. has been produced. The DPD of polyTHF (trace (b)) is also narrow with the peak maximum at 10,000 M.W. but being signalled principally by the D.R. detector; the very small U.V. absorption is due to the benzyl moiety from the initiator. It is evident from the trace of the reaction products, (c), that the bulk of the poly(α-methylstyrene) remains as the homopolymer, although some block copolymer has been formed as evinced by the increase in U.V. absorption appearing at 10,000 M.W. There is no conclusive evidence of any broadening of the curves towards higher molecular weight owing to the presence of 15,000 M.W. block copolymer, but the logarithmic relationship of the D.R. base line of the g.p.c. trace with molecular weight makes this a very insensitive diagnostic tool. It may be estimated roughly from the shape of the U.V. trace of the product that about 20-30% of the reaction between living poly(α-methylstyrene) and living polyTHF is additive.

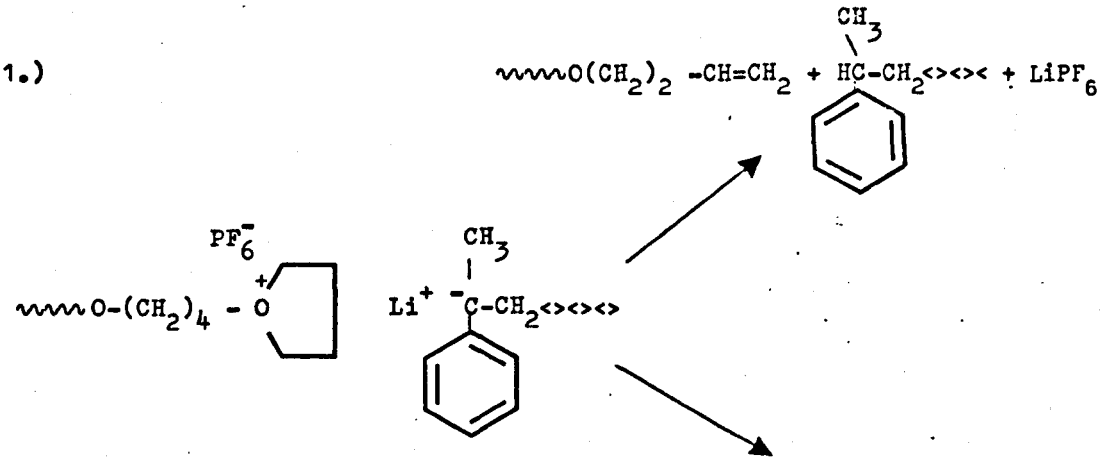
The fact that the U.V. signal strength of the residual homopoly(α-methylstyrene) approximates to that of the protonated sample (trace (a)), indicates strongly that the reaction causing formation of homopolymer is a β-proton transfer from the living

FIGURE 3.3.4.

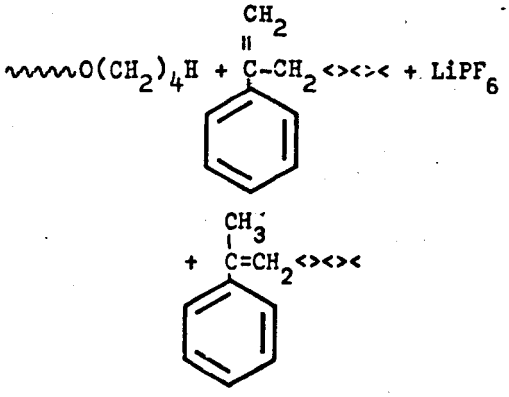


Gpc traces of (a) methanol terminated poly(α-methylstyrene), (b) methanol terminated polyTHF, and (c) the products of the reaction of living poly(α-methylstyrene) and living polyTHF at 195K.

(3.1.)



(3.2.)

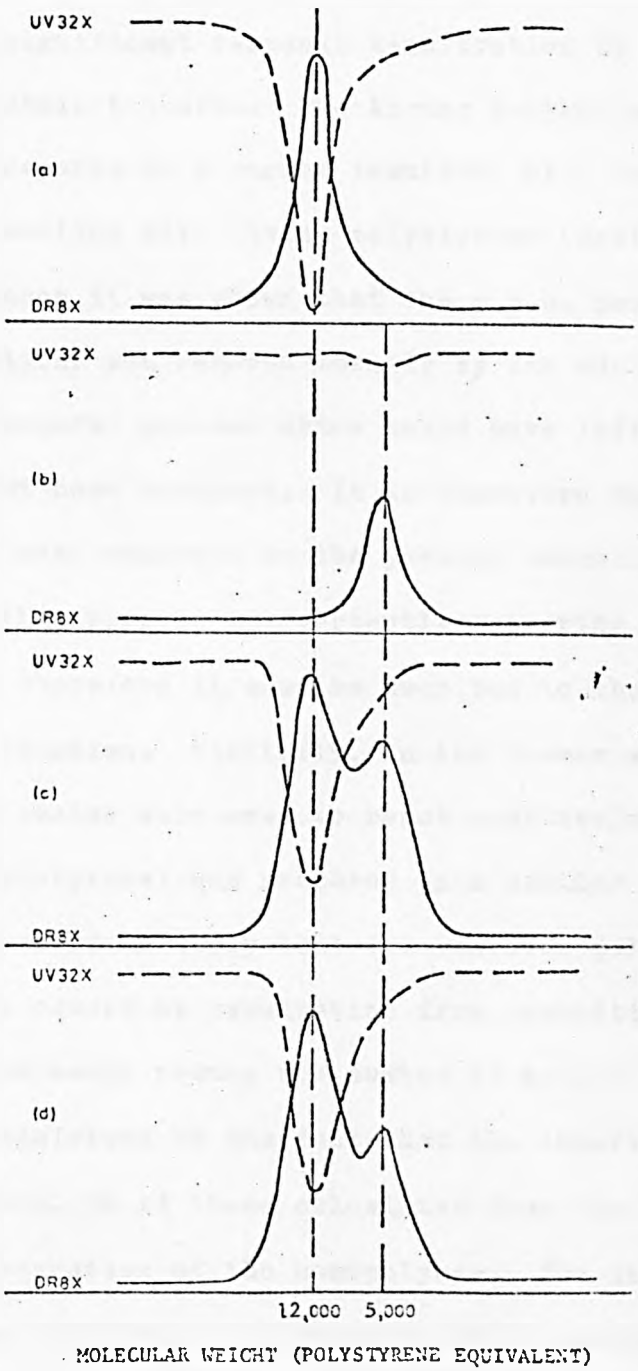


polyTHF to the poly(α-methylstyryl) anion, (equation (3.1.)) rather than hydride transfer (equation (3.2.)). The argument is this: If reaction (3.2.) were to occur, then the resultant substituted styryl units would have a very high extinction coefficient at 254nm and so their existence should have been indicated by a greatly enhanced U.V. absorption. Styrene monomer has an extinction coefficient at 254nm approximately two orders of magnitude greater than that of ethylbenzene.[10] No such increase is recorded on trace (c) and so this alternative reaction may be neglected.

Similar results were obtained from the experiment recorded in Figure 3.3.5. In this instance the molecular weight of the polyTHF was less than that of the poly(α-methylstyrene) so that block copolymer formation is only shown by a drop in the U.V.:D.R. ratio at 12,000 M.W. for the product relative to homopoly(α-methylstyrene). Residual polyTHF is shown as a low molecular weight shoulder by the D.R. detector and is unobserved by the U.V. detector. This product trace is also consistent with an estimate of the addition process being about 20-30% efficient.

The fourth trace (d) in Figure 3.3.5. is of the product which resulted from the reaction of living polyTHF with poly(α-methylstyrene) after the latter had been converted into a polymeric Grignard reagent. It was thought that a reduction in the basicity of this component polymer could influence the relative probabilities of the addition and metathetical reaction processes. From examination of the traces (c) and (d) it appeared that there was some small but significant increase in linking obtained by use of the Grignard-terminated reagent and so investigations were continued on this modification with the di-Grignard terminated α-methylstyrene tetramer and living

FIGURE 3.3.5.



Gpc traces of (a) methanol terminated poly(α-methylstyrene), (b) methanol terminated polyTHF, (c) the products of the reaction of living poly-(α-methylstyrene) and living polyTHF at 195K and (d) the products of the reaction of poly(α-methylstyrene) Grignard and living polyTHF at 195K.

polyTHF (see section 3.2.3.).

The inferences drawn about the efficiency of linking with poly(α-MS) depend entirely on the assumption that all the chains possess active ends and that there is no significant terminal deactivation by spurious impurities or by chain transfer. The living polyTHF generated for this study was prepared in a manner identical with that used in the study of its reaction with living polystyrene (section 3.2.1.). In this circumstance it was shown that the g.p.c. peak associated with the homopolyTHF was removed totally by the addition reaction so that a chain transfer process which would have left unreactive polyTHF could not have occurred. It is therefore very unlikely that the residual peak observed in the present investigation can be attributed to this process inadvertently occurring due to experimental faults and therefore it must be ascribed to the product of a metathetical reaction. Similarly, in the former work all the living polystyrene chains were seen to react additively and, as the living poly (α-methylstyrene) was prepared in a similar if not identical way, it also seems unlikely that the residual poly(α-methylstyrene) observed was caused by termination from impurities. Since a termination reaction would reduce the number of active ends, the latter conclusion is reinforced by the fact that the observed titration figures were within ± 3% of those calculated from the amounts of catalysts used in the generation of the homopolymer. The interpretation of the results as indicating the presence of a pronounced proton abstraction in the system must therefore be valid.

Although the study of the poly(α-methylstyrene)-polyTHF reaction could have been made more quantitative by choosing molecular weights for the component polymers sufficiently far apart for there to be no

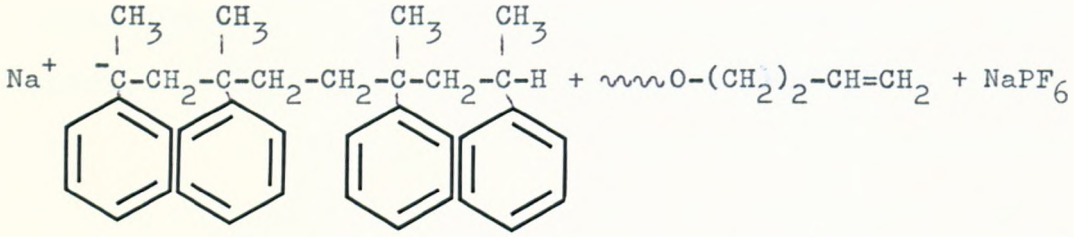
appreciable overlap in the g.p.c. traces of the products, this method suffers from the overall limitation that the reaction is carried out at low temperatures to avoid depropagation of the anionic reagent, and so it is difficult to obtain a temperature profile of the process. This problem can be avoided if the reaction between living polyTHF and the difunctional living α-methylstyrene tetramer is examined instead.

3.2.3. α-Methylstyrene tetramer and living polyTHF

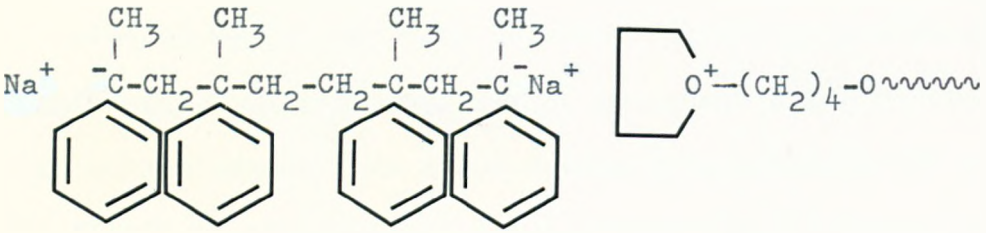
A study was undertaken with these reagents to find (i) the percentage of block copolymerisation and (ii) the activation energy difference between the desired linking reaction and the competitive non-linking reaction.

The main advantage with the tetramer over the poly(α-methylstyrene) is that it may be prepared as a unique species by reacting the monomer in THF directly with sodium metal at a concentration of the former just below that characteristic of the monomer in equilibrium with its own living polymer at the chosen reaction temperature. Once prepared (e.g. at 273K) it can be used as a stable reagent over a range of temperatures without introducing difficulties due to its depropagation. The structure of the tetramer (equation (1.9.))is a good model for that of the reaction product from the polymer since the terminal units are linked as in the polymer in the head-tail mode.

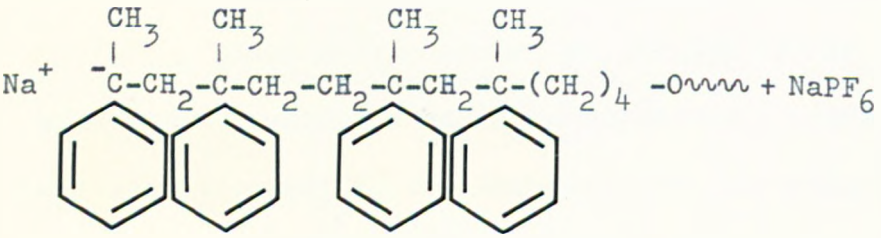
Initially, however, experiments with the tetramer were used to confirm that the metathetical reaction was one of proton rather than hydride transfer. The former reaction requires that the α-methylstyrene product should be the diprotonated adduct, whereas the latter would yield a tetramer with terminal unsaturation at both ends.



(3.4.)



(3.3.)



The diprotonated material has been prepared on previous occasions[75,76.] and so authentic samples were available for comparison purposes.

The product of the reaction between the tetramer and low molecular weight polyTHF was isolated and subjected to g.l.c. analysis and separation for p.m.r. identification. The first peak in the g.l.c. trace was shown to have a retention time identical with that of the authentic sample, and its structure was confirmed as being the diprotonated material by p.m.r.; there were no absorptions corresponding to vinylic protons in the spectrum. Thus the predominating reaction is a β-proton transfer.

If zero order statistics apply, in which the probability of the way a given polymer end will react is independent of the mode of reaction or non-reaction of the other end, then the probability of proton transfer, P (equations (3.3.) and (3.4.)) may be evaluated from the U.V. traces of the g.p.c. in the following way: The probabilities of forming ABA copolymer, AB copolymer, homopolyTHF and tetramer are $(1-P)^2$, $2P(1-P)$, P and P^2 respectively. Therefore, from the g.p.c. traces the ratio of the number of those tetramer units incorporated into the copolymer (as AB and ABA copolymers) to the number of those remaining unreacted can be measured and described by the ratio $(1-P)^2:P^2$ from which P can be obtained. Table 3.3. illustrates some of the results that were obtained from the g.p.c. curves. The value of P is a measure of the probability of proton transfer occurring, hence (1-P) is the fraction of block copolymer produced.

It is implied in equations (3.3.) and (3.4.) that the two competing reactions proceed via a similar path in which the order of reaction with respect to the components is the same. If this be so, then the value of P should be independent of the relative concen-

TABLE 3.3

REACTION OF α_4^- (100% ADDITION) WITH LIVING POLYTHF.[SK38]

Temperature (T) K	$(10^3/T)/K^{-1}$	uv area of α_4H_2	uv area of copolymer	Total	P	$\log(\frac{1}{P}-1)$
263	3.80	18.4	11.6	30.0	0.78	-0.549
253	3.95	19.4	12.5	31.9	0.78	-0.549
223	4.48	20.2	12.0	32.2	0.79	-0.568
195	5.13	20.7	11.7	32.4	0.80	-0.602

Graph 3.3 shows a plot of log(1/P-1) vs. 1/T.

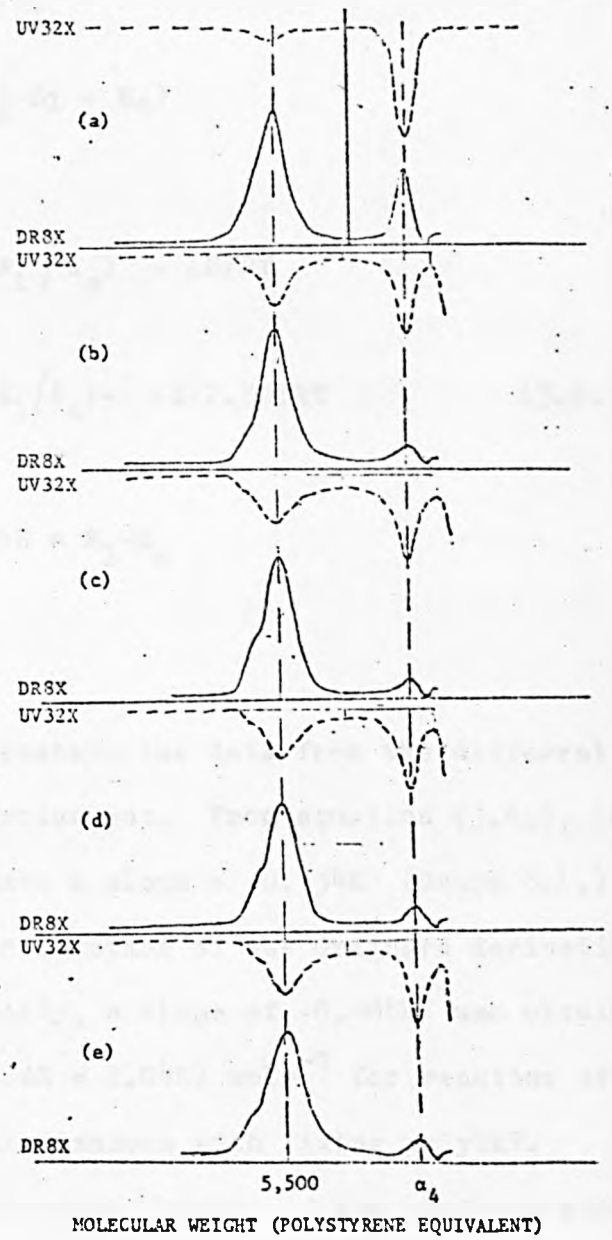
trations of the reagents, and this was checked by deriving the values from samples where only 50% of the calculated amount of living tetramer had been added to the living polyTHF,and the remaining ends were terminated with methanol. The g.p.c. traces for this reaction are shown in Figure 3.3.6. It is obvious from the different traces that some tetramer has been incorporated into block copolymer as indicated by the increase in U.V. intensity for polyTHF, and its decrease for tetramer. The P values calculated for the various experiments are approximately the same within experimental accuracy (Tables 3.3.-3.5.). Therefore, no change in the probability of the proton transfer reaction occurs as the relative concentrations of reagents is changed.

In practice the U.V. traces did not return to the base line between the peaks or at the low molecular weight end and so verticals were dropped at the absorption minima as shown in Figures 3.3.6. and 3.3.7., in order to estimate the areas. This procedure introduces some inaccuracy into the absolute values of the probabilities derived from these measurements, but as similar traces were obtained for, and similar procedures were applied to, the products of the reaction at other temperatures, internal consistency was probably achieved in measuring the temperature profile of this system.

To find the activation energy difference (Δ E), the difference between the activation energy for the proton transfer reaction and the linking reaction, it was necessary to obtain first the value for P and make the following assumption (equation (3.5.));

$$P = k_a / (k_a + k_1) \qquad (3.5.)$$

FIGURE 3.3.6



G.p.c. traces of (a) methoxy-terminated monofunctional polyTHF and protonated α-methylstyrene α_4 (combined trace from two separate traces), and the products of the 50% reaction between thesettwo living species at (b) 195K, (c) 223K, (d) 253K, (e) 263K.

where K_a is the rate constant for the proton transfer process, and K_1 is the rate constant for the coupling reaction.

$$1/P = 1 + A_1 e^{-E_1/RT} \Big/ A_a e^{-E_a/RT}$$

$$1/P = 1 + (A_1/A_a) e^{(-E_1 + E_a)}$$

$$\ln(1/p-1) = \ln (A_1/A_a) - \Delta E/RT$$

$$\log_{10}(1/P-1) \log(A_1/A_a) - \Delta E/2.303RT \qquad (3.6.)$$

$$\text{where} \quad \Delta E = E_1 - E_a$$

Tables 3.3., 3.4. and 3.5. contain the data from the different sets of experiments that were carried out. From equation (3.6.), the plot of $\log_{10}(1/P-1)$vs 1/T gave a slope = -0.134K (Graph 3.1.) and hence ΔE = 2.5KJ $mole^{-1}$ for reaction of the Grignard derivative with living polyTHF. Similarly, a slope of -0.108K was obtained from Graph 3.2., and hence ΔE = 2.04KJ $mole^{-1}$ for reaction of the α-methylstyrene tetramer dianions with living polyTHF.

Figure 3.3.7. shows the g.p.c. traces of the products obtained from 100% addition of the stoichiometric volume of living tetramer and the trends observed are identical to those recorded for the 50% reaction (Figure 3.3.6.). On comparison of the P values derived from the two types of reaction (Tables 3.3. and 3.5.), they are, within experimental error, in close agreement and consistently

TABLE 3.4.

REACTION OF $\alpha_4(MgBr)_2$ (100% ADDITION) WITH LIVING POLYTHF.[SK36]

TEMPERATURE / K	$(10^3/T)/K^{-1}$	P	$\log(\frac{1}{P}-1)$
263	3.80	0.63	-0.229
253	3.95	0.68	-0.328
195	5.13	0.74	-0.456

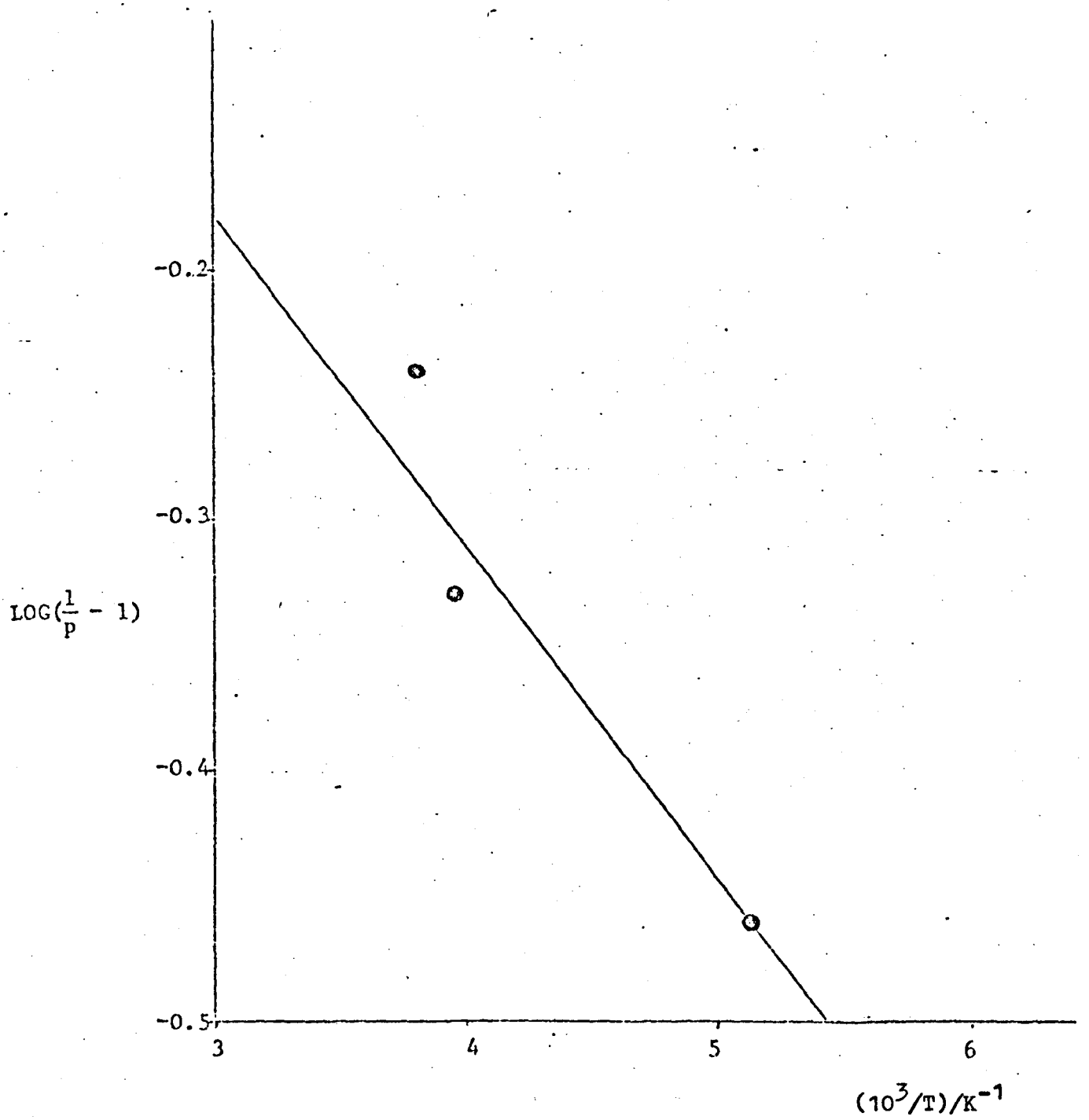
TABLE 3.5.

REACTION OF $\alpha_4^{=}$ (50% ADDITION) WITH LIVING POLYTHF.[SK37]

TEMPERATURE / K	$(10^3/T)/K^{-1}$	P	$\log(\frac{1}{P}-1)$
263	3.80	0,76	-0.500
253	3.95	0.80	-0.602
223	4.48	0.81	-0.629
195	5.13	0.81	-0.629

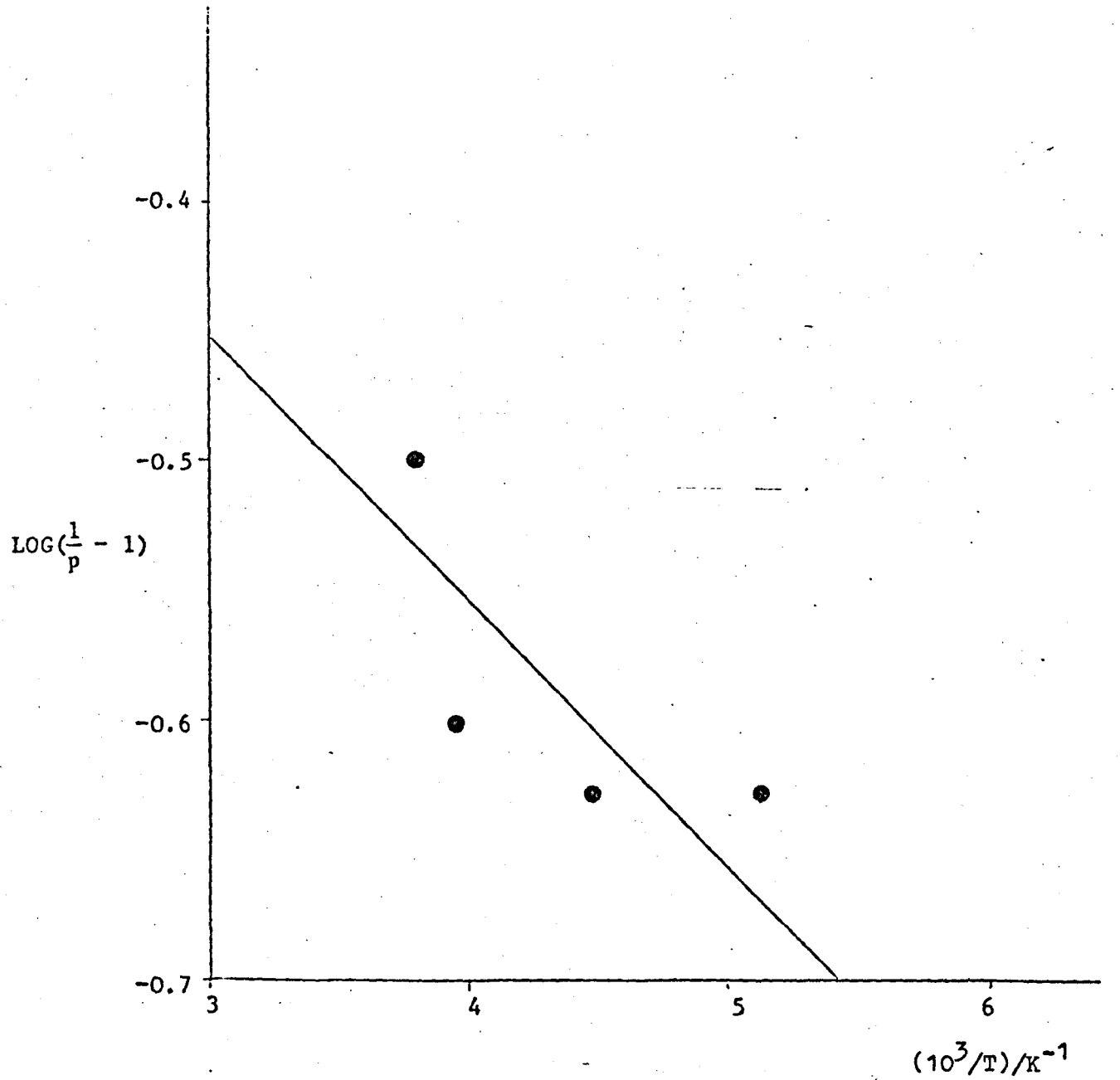
GRAPH 3.1

A PLOT OF LOG$(\frac{1}{p} - 1)$ vs $\frac{1}{T}$ FOR THE GRIGNARD TERMINATED $\alpha_4^{=}$/PTHF^{+} REACTION.



GRAPH 3.2

A PLOT OF LOG($\frac{1}{P}$ - 1) vs $\frac{1}{T}$ FOR THE $\alpha_4^{=}$ (50% ADDITION) /PTHF$^+$ REACTION.



GRAPH 3.3

A PLOT OF LOG$(\frac{1}{p} - 1)$ vs $\frac{1}{T}$ FOR THE $\alpha_4^=$ (100% ADDITION) /PTHF$^+$ REACTION.

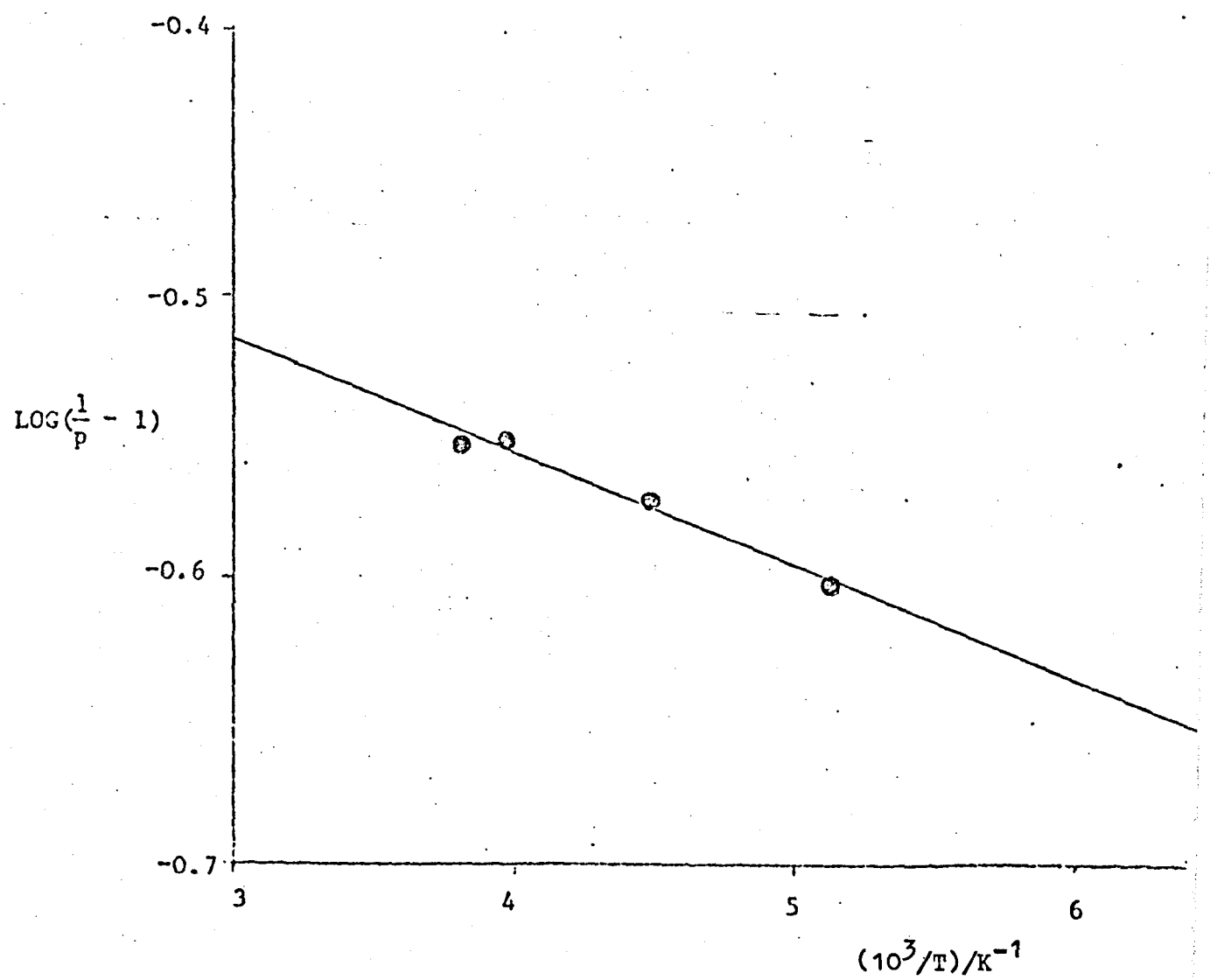
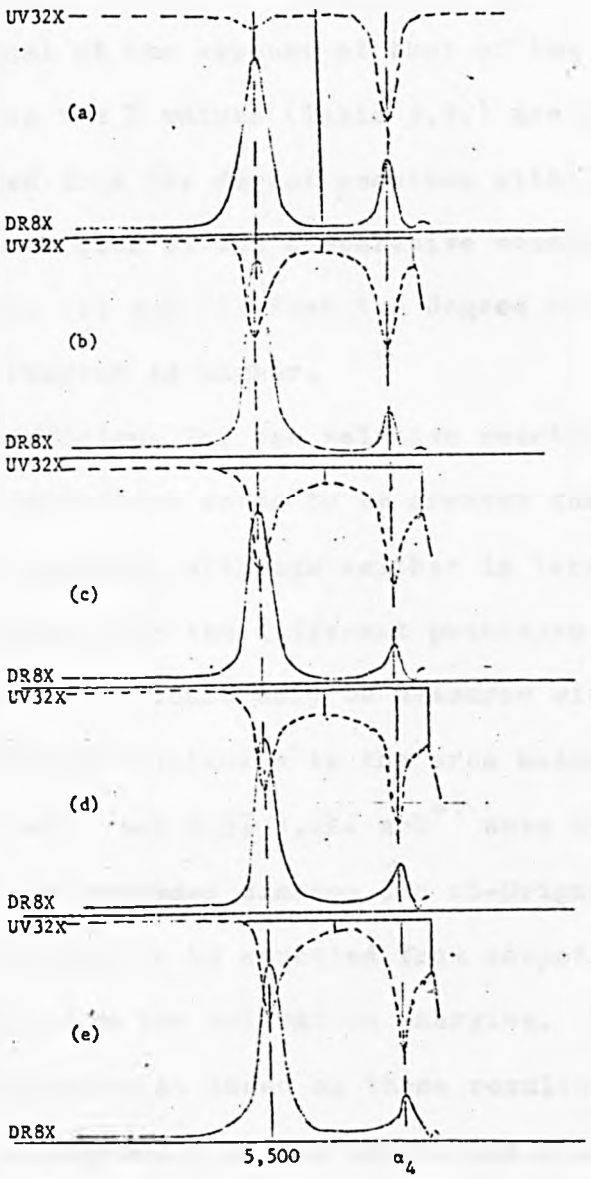


FIGURE 3.3.7.



MOLECULAR WEIGHT (POLYSTYRENE EQUIVALENT)

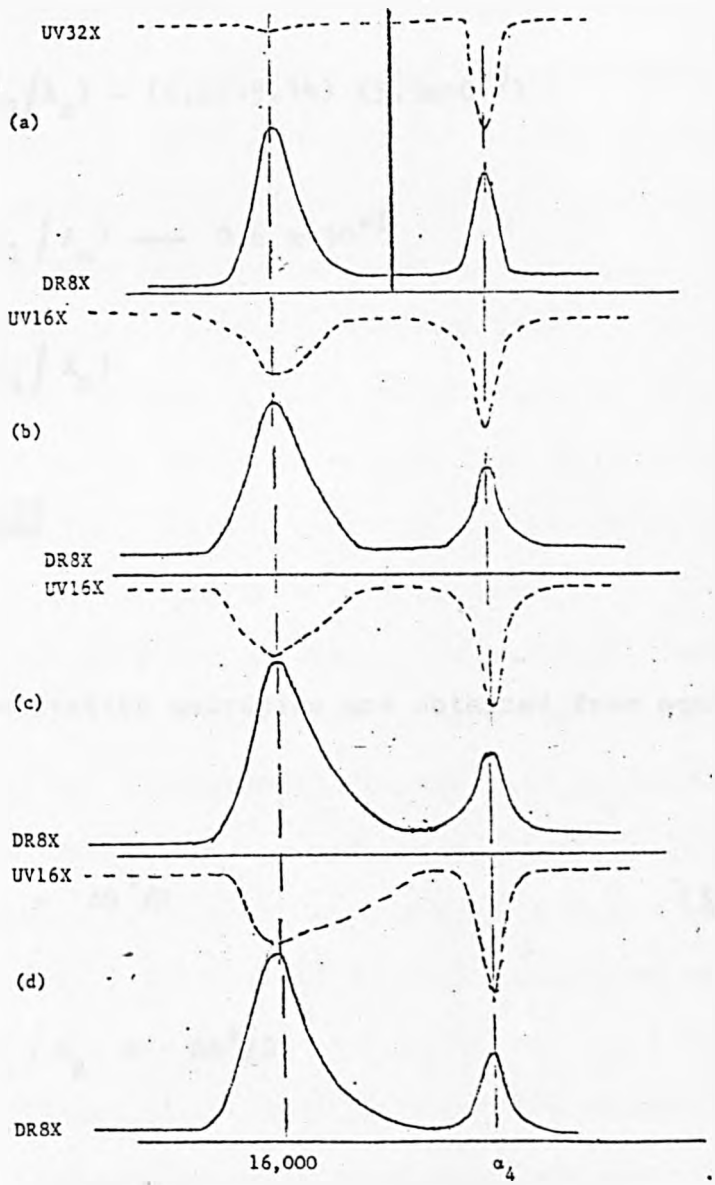
G.p.c. traces of (a) methoxy-terminated monofunctional polyTHF and protonated α-methylstyrene tetramer (combined trace from two separate traces), and the products of the 100% reaction between these two living species at (b) 195K, (c) 223K, (d) 253K, and (e) 263K.

indicate a 20% yield of block copolymer.

Figure 3.3.8. records the g.p.c. traces of the products from the reaction which involved the di-Grignard tetramer derivative and living polyTHF. The U.V. absorption pattern is the same as in the previous experiments (Figures 3.3.6. and 3.3.7.); with enhancement of the polyTHF U.V. signal at the expense of that of the tetramer. However, in this instance the P values (Table 3.4.) are significantly lower than those obtained from the direct reaction with the dianion and so confirmation can be made of the comparative observations recorded in Figure 3.3.5. (c) and (d) that the degree of linking with the polymeric Grignard reagent is higher.

The temperature coefficient for the relative reaction rates involving the Grignard derivative seems to be greater than that observed in the direct reaction, although neither is large. The activation energy difference for the different processes (obtained from the Graphs 3.1. and 3.2.) could only be measured within wide limits because of inherent inaccuracies in the area measurements, but figures of 2.04 ± 1.2KJ mol^{-1} and 2.5 ± 1.2KJ mol^{-1} were obtained for the reaction involving the tetramer dianion and di-Grignard respectively. These low values are to be expected from competitive reactions which individually have low activation energies. Perhaps the only safe conclusion to arrive at based on these results is that the addition reaction has a marginally higher activation energy than the metathetical reaction. This seems reasonable when it is realised that the former process requires replacement of a tightly co-ordinated THF molecule (equation (3.3.)) whereas the latter involves the elimination of a proton bound to the β-carbon atom by a bond weakened by the proximity of the oxonium ion (equation (3.4.)). The activation

FIGURE 3.3.8.



MOLECULAR WEIGHT (POLYSTYRENE EQUIVALENT)

G.p.c. traces of (a) methoxy-terminated monofunctional polyTHF and Grignard terminated α-methylstyrene tetramer (combined trace from two separate traces), and the products of the 100% reaction of these species at (b) 195K, (c) 253K, and (d) 263K.

entropy differences ($\Delta\Delta S^{\ddagger}$) and the pre-exponential factors of the two different processes are derived by the calculation outlined below: For the di-Grignard tetramer and living polyTHF.

$$\log(1/P-1) = \log(A_1/A_a) - \Delta E/2.303x8.314T \qquad (3.6.)$$

$$-0.48 = \log(A_1/A_a) - (2.5/19.14)\ (5.3x10^{-3})$$

$$-0.48 = \log(A_1/A_a) - 0.6 \times 10^{-3}$$

$$-0.48 = \log(A_1/A_a)$$

$$(A_1/A_a) = \underline{\underline{0.33}}$$

The differences in activation entropies are obtained from equation (3.6.).

$$\ln A_1 - \ln A_a = \Delta S^{\ddagger}/R \qquad (3.7.)$$

$$2.303 \log A_1/A_a = \Delta S^{\ddagger}/R$$

If $A_1/A_a = 0.33$,

$$2.303 \times 8.314 \times \log 0.33 = \Delta S^{\ddagger}$$
$$19.14 \times (-0.4815) = \Delta S^{\ddagger}$$
$$\Delta S^{\ddagger} = \underline{\underline{-9.3JK^{-1}\ mol^{-1}}}$$

Table 3.6. lists the values of $\Delta\Delta S^{\ddagger}$ for the 100% and 50% stoichiometric addition of living α-methylstyrene tetramer to living polyTHF.

The activation entropy difference ($\Delta\Delta S^{\ddagger}$) is negative because the pre-exponential factor for the proton transfer reaction (A_a) is greater than that for linking (A_l), but no conclusion can be drawn about the transition state complex from these data. The reliability of the results for (A_l/A_a) is uncertain since the experimental method of determination has inherent errors, (e.g. the measurement of peak areas); the values of $\Delta\Delta S^{\ddagger}$ describe a difference in the degrees of freedom in the transition complexes in the two reactions.

The marked difference in behaviour between living polystyrene and living poly(α-methylstyrene) in their reactions with living poly THF must be commented upon. It is unexpected that the introduction of a methyl group onto the terminal carbanion of the chain should reduce the efficiency of linking from 100% to about 20%. Although the presence of the methyl group increases the nucleophilicity of the carbanion, and the experiments with Grignard derivatives indicate that a reduction in this property enhances the probability of addition, it seems unlikely that this degree of change in reactivity is sufficient to account for a drop of this magnitude in the linking efficiency. It is perhaps more likely that the increased steric hinderance resulting from the methyl group renders attack at the oxonium ion more difficult and thereby enhances the probability of reaction at the more accessible β-carbon atom. This postulate is, however, only partially supported by examination of molecular models. Additional evidence for the steric hindrance concept may be obtained from reaction of living 1,1-diphenylethylene with living polyTHF (section 3.2.4.). In this system there appears to be no addition reaction and this can be interpreted as being due to the

TABLE 3.6.

THERMODYNAMIC DATA FOR THE LIVING TETRAMER-LIVING POLYTHF SYSTEM

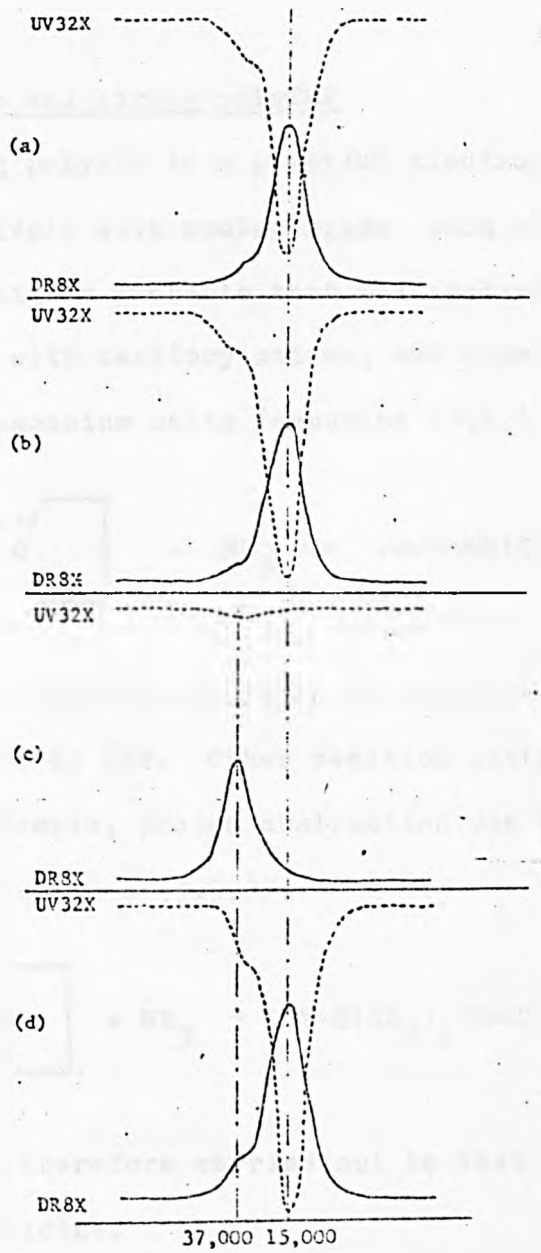
$\%\alpha_4^-$ ADDED	A_1/A_a	$\Delta\Delta S^{\ddagger}$ ($JK^{-1}mol^{-1}$)
100	0.25	-11.5
50	0.32	-9.5

two phenyl groups blocking completely the attack by the strongly nucleophilic carbanion at the oxonium ion. Molecular models of the system are consistent with this analysis.

3.2.4. Living 1,1-diphenylethylene and living polyTHF

Figure 3.3.9. shows the g.p.c. traces of the homopolymer components and the products of their mutual reaction.Trace (a) is of the methanol terminated polystyrene before addition of the 1,1,-diphenylethylene. Trace (b) is of the sample protonated after the addition of 1,1-diphenylethylene, and in this the U.V. signal is enhanced in comparison with trace (a) because of the 1,1-diphenylethylene at the end of the chain. Trace (c) is of a methanol-terminated sample of the polyTHF used for the linking reaction. Trace (d) which is of the product obtained from reaction of the homopolymers shows little difference from that expected by superposition of traces (b) and (c), with no movement of the peak to higher molecular weights. However, the shoulder present on the high molecular weight tail of both the protonated anionic samples is more defined and pronounced in trace (d), and thus a very small amount of linking cannot be ruled out.Although the signal from the homopolyTHF is buried under the high molecular weight region of the product trace and further experiments are required in which the molecular weights of the homopolymers are selected to have widely differing retention times before the degree of linking can be quantified, it is evident from this experiment that it is extremely small. Since all the techniques and precautions used in the preparations and the titration of the homopolymers were identical to those used in the polystyrene studies , it is unlikely that inadvertent

FIGURE 3.3.9.

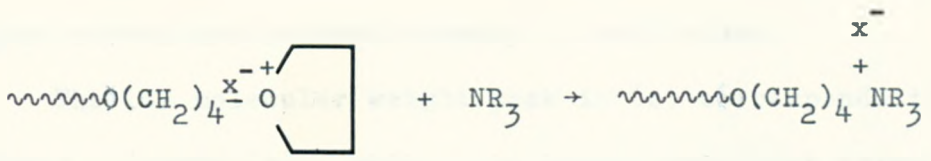


G.p.c. traces of (a) protonated monofunctional polystyrene, (b) 1,1-diphenylethylene terminated monofunctional polystyrene, (c) methoxy terminated monofunctional polyTHF, and (c) the product of the reaction between these two living polymers.

termination of the samples by impurities is the cause of the lack of linking observed. It is therefore far more probable that steric hindrance prevents the linking reaction in favour of the alternative proton transfer.

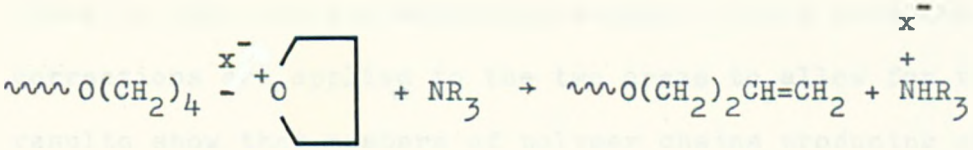
3.2.5. Pyridine and living polyTHF

Since living polyTHF is a powerful electrophilic reagent which reacts quantitatively with nucleophiles such as sodium phenoxide[77], it seemed to be highly probable that this polymeric system would react additively with tertiary amines, and especially pyridine, to form quaternary ammonium salts (equation (3.8.)).



(3.8.)

This replacement reaction should occur whenever the basicity of the amine exceeds that of THF. Other reaction pathways are, of course, possible. For example, proton abstraction can in theory also occur in this system (equation (3.9.)).



(3.9.)

Experiments were therefore carried out to test the efficiency of this reaction with pyridine.

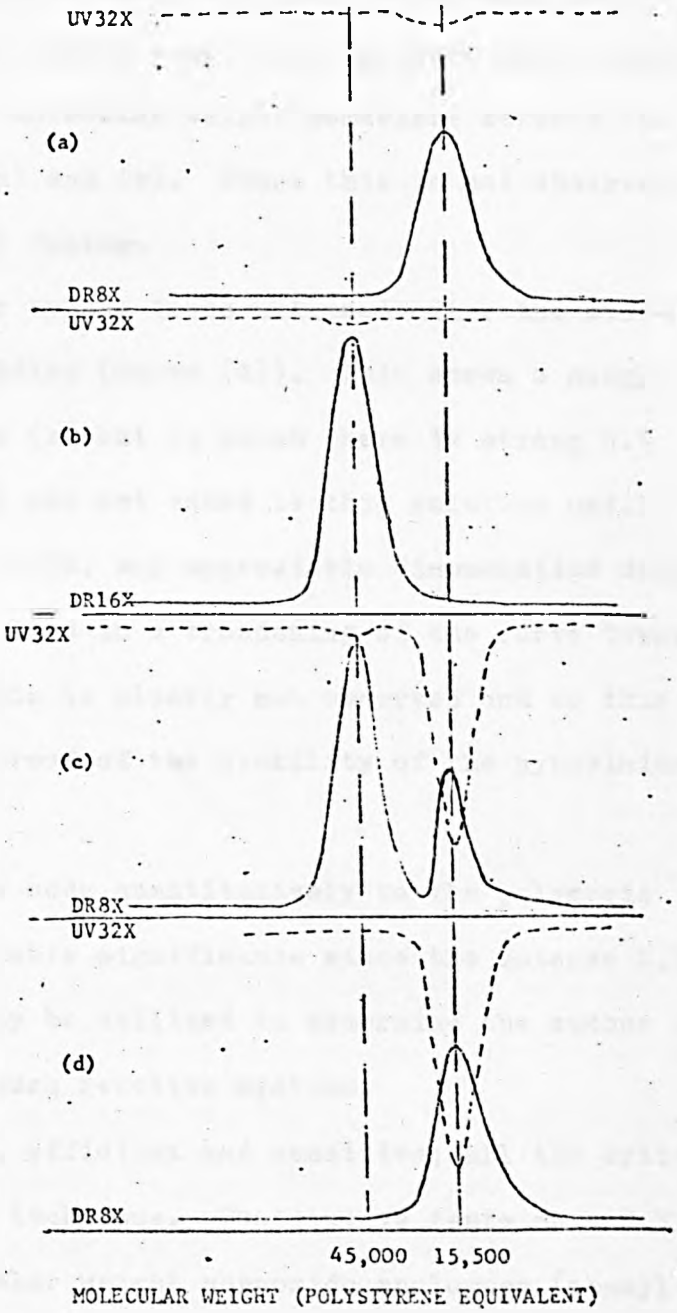
The following experiment is typical of a number carried out to evaluate this reaction. The polymerisation of THF was initiated under living conditions with benzyl bromide as co-initiator. After three hours three samples, A, B, and C were removed; A was terminated with methanol, B was reacted with half the stoichiometric amount of

pyridine required to terminate the living ends, and C was reacted with a stoichiometric amount of pyridine. Sample B was then left to polymerise for a further three hours at 263K before it was terminated with methanol. The g.p.c. traces of the products are recorded in Figure 3.3.10. Curves (a) and (b) represent the trace obtained after killing the THF polymerisation with methanol after three and six hours respectively. Curve (c) is the trace of sample B to which the 50% stoichiometric amount of pyridine had been added after three hours and the solution had been terminated with methanol after six hours, and curve (d) shows the product after stoichiometric reaction with pyridine after three hours. It is clear that these curves are related closely to each other.

The low molecular weight peak in (c) corresponds to that of sample A (curve (a)), whilst the higher molecular weight peak corresponds to that of sample C (curve (b)). Furthermore, the former peak shows an intense U.V. signal which can only be ascribed to a pyridine adduct. The areas of the two curves shown by the differential refractometer trace in curve (c) are related to each other by the relative molecular weights of the products. When corrections are applied to the two areas to allow for this, the results show that numbers of polymer chains producing each curve are approximately equal (number of low M.W. chains: number of high M.W. chains = 0.98 ± 0.005).

These results are very significant since they show that (a) the reaction between living polyTHF and pyridine is exclusively additive; (b) the reaction is quantitative; (c) the adduct is too stable to participate any further in the polymerisation process; (d) there is no exchange between the adduct and the excess of polyTHF

FIGURE 3.3.10.



G.p.c. traces of (a) methoxy terminated monofunctional living polyTHF withdrawn after 3 hours, (b) methoxy terminated monofunctional living polyTHF withdrawn after 6 hours, (c) pyridine (50%) terminated monofunctional living polyTHF and (d) pyridine (100%) terminated monofunctional living polyTHF.

oxonium ions. The last two points are related and need to be developed a little further. If the quaternary ammonium (pyridinium) salt were only formed as the product of an equilibrium in which significant amounts of pyridine remained, then the dynamic nature of this equilibrium process should result in a product which would exhibit a single peak at a molecular weight somewhere between the extremes shown by curves (a) and (b). Since this is not observed, the conclusions (c) and (d) follow.

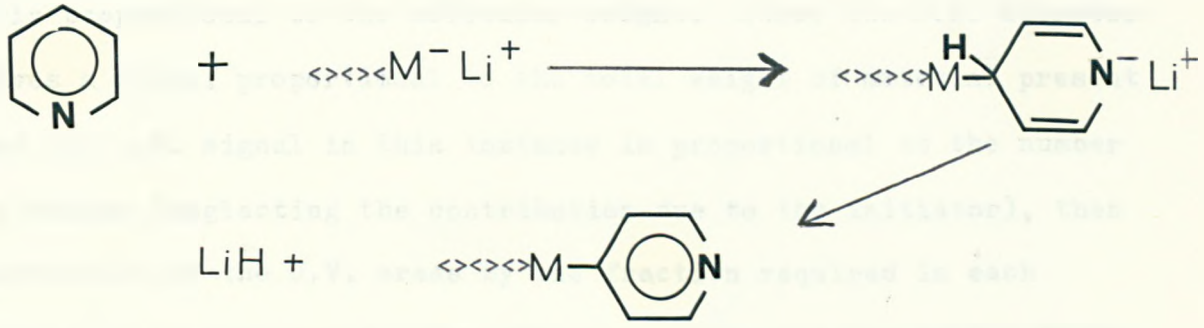
This view is supported by the trace obtained after the stoichiometric addition of pyridine (curve (d)). This shows a single peak corresponding to curve (a) but in which there is strong U.V. absorbance. Since methanol was not added to this solution until three hours had elapsed at 263K, any appreciable dissociation during this period would have resulted in a broadening of the curve toward high molecular weights. This is clearly not observed and so this trace constitutes further proof of the stability of the pyridinium salt formed.

The fact that pyridine adds quantitatively to the polymeric oxonium ions is of considerable significance since the intense U.V. absorbance of the adduct may be utilized to determine the number of active species present in such reactive systems.

The process is simple, efficient and sensitive; all the criteria demanded for an analytical technique. Qualitative tests on a U.V. instrument using low molecular weight phenoxide analogues (phenyl methyl ether and phenyl ethyl ether) and pyridine terminated polyTHF have shown that the pyridine system exhibits a U.V. signal at 254nm (the fixed wavelength at which a g.p.c. instrument operates) greater by a factor approaching ten. Phenoxides were chosen as a suitable

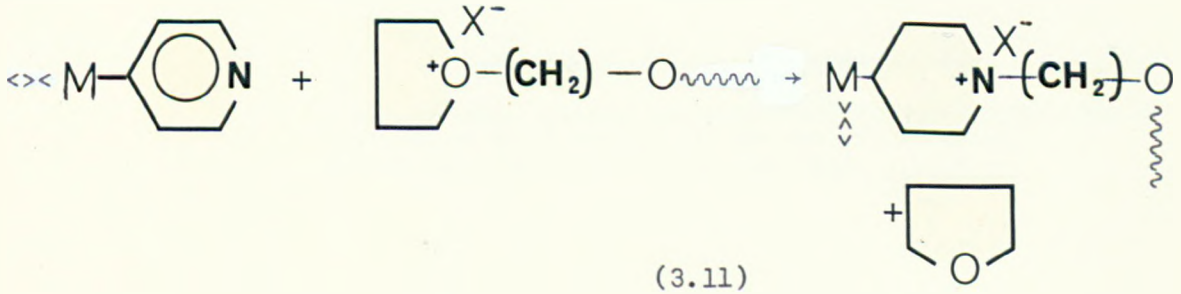
comparison because of their established use as reagents for determining the number of active ends[77]. Therefore, pyridine offers the opportunity of providing an easier and more sensitive guide in the detection of active end concentration in such polymerisations.

Other uses for pyridine terminated polymers are now being studied by Richards' group at Waltham Abbey. One such investigation is based on the fact, previously discovered by this group, that pyridine may be added to living polybutadiene to form an adduct which could then be re-aromatised thermally to yield a 4-polybutadiene-pyridine, as shown in equation (3.10):



(3.10)

Experiments are currently being conducted to react this material with living polyTHF in order to form block copolymers in which the links between blocks are ionic (equation (3.11.)). Such materials should have interesting morphologies since the polymeric components are incompatible with each other and both are incompatible with the ionic linking group.



(3.11)

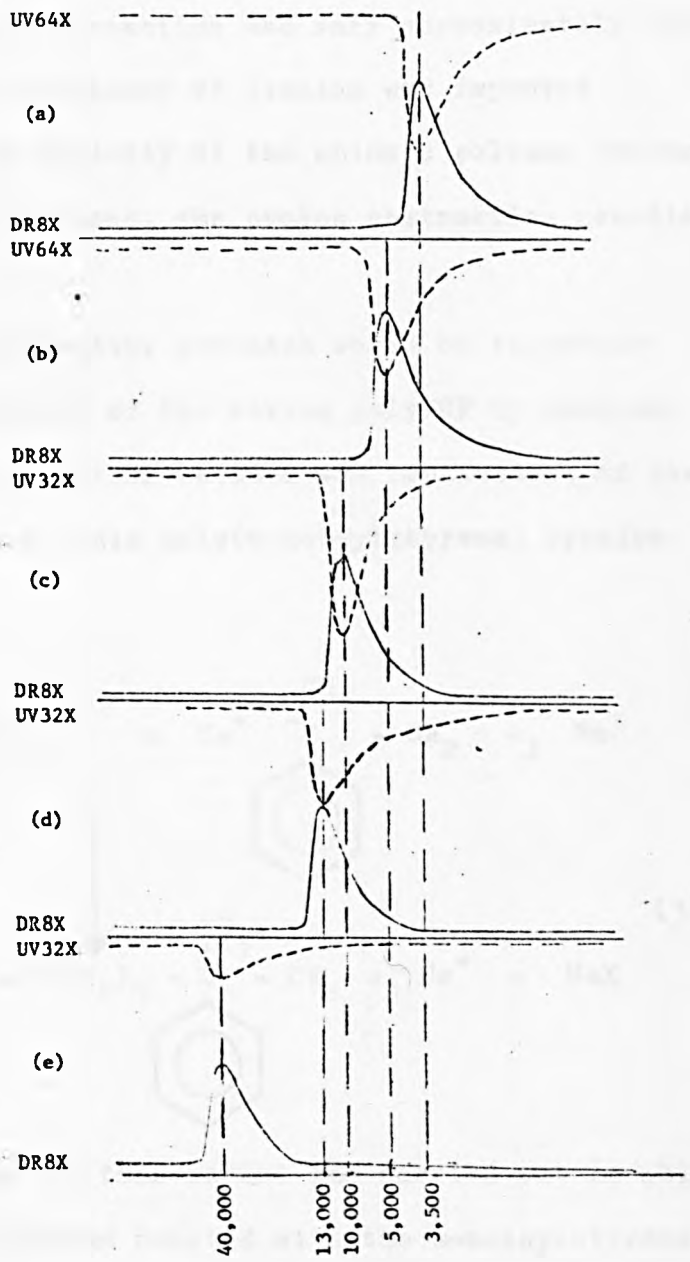
Other work is also being carried out to study the efficiencies of the reactions of polymeric cations with other tertiary amines.

The usefulness of this reaction as an analytical tool to determine the number of active species present rests on the assumption of proportionality of U.V. optical density at 254nm and the concentration of active species. This was examined qualitatively by allowing THF to be polymerised under living conditions and extracting samples at increasing time to be killed with pyridine. The products were then examined by g.p.c.

In this exploratory experiment advantage was taken of the fact that at constant weight the number of polymeric ends is inversely proportional to the molecular weight. Since the D.R. detector gives a signal proportional to the total weight of material present and the U.V. signal in this instance is proportional to the number of chains (neglecting the contribution due to the initiator), then correction of the U.V. areas by the fraction required in each sample to normalise the D.R. area to a constant value should yield values which can be plotted against polymer molecular weight to test applicability of the Beer-Lambert Law in this system. However, the experiment was too inaccurate for any quantitative measurements to be made from the g.p.c. traces.

The traces obtained during the reaction are shown in Figure 3.3.11. and it can be seen qualitatively that the U.V. signal decreases with increasing polymer molecular weight.

FIGURE 3.3.11.



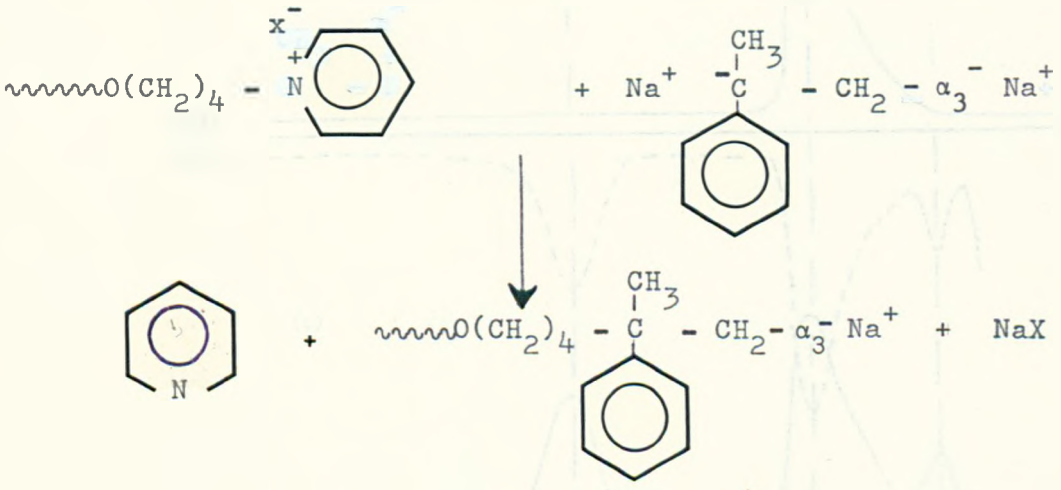
MOLECULAR WEIGHT (POLYSTYRENE EQUIVALENT)

G.p.c. traces of pyridine terminated monofunctional polyTHF after reaction for (a) 40 minutes, (b) one hour, (c) two hours, (d) two and a half-hours, and (e) six hours.

3.2.6. Pyridine terminated polyTHF and living α-methylstyrene tetramer

In the experiments involving the direct reaction of polymeric anions with living polyTHF it was shown that with living poly (α-methylstyrene) the linking reaction was only approximately 20% efficient. Although the efficiency of linking was improved marginally by reducing the basicity of the anionic polymer through the formation of Grignard reagent, the proton abstraction reaction still predominated.

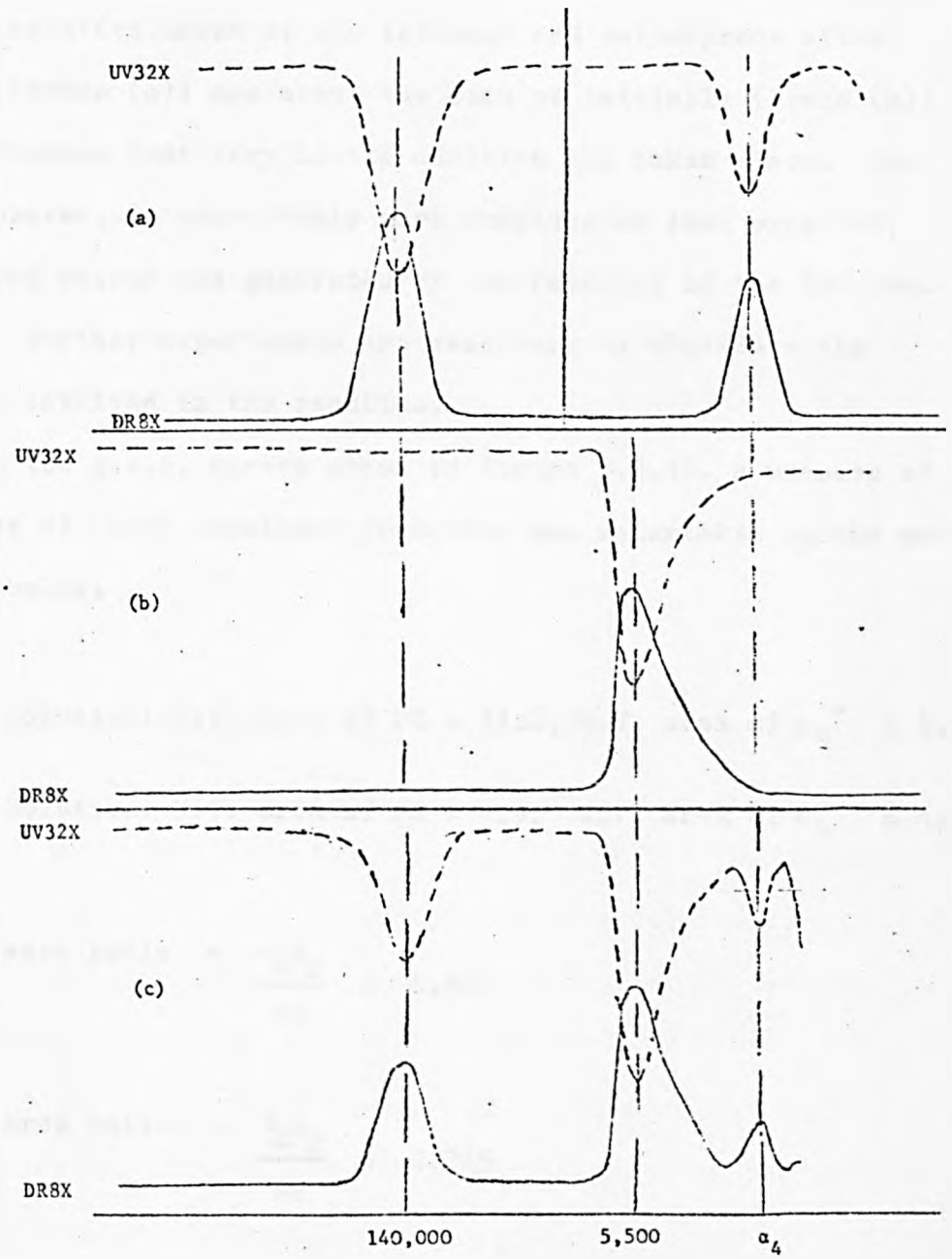
It seemed that an alternative approach would be to reduce initially the electrophilicity of the living polyTHF by complexation with pyridine. The reaction devised was replacement of the pyridine moiety by the more basic poly(α-methylstyrene) species (equation (3.12.).



(3.12)

Accordingly, an experiment of this nature was carried out in which pyridine-terminated polyTHF was reacted with the α-methylstyrene tetramer dianion ($\alpha_4^{=}$). The g.p.c. traces of the products of such experiments are shown in Figure 3.3.12. Because of the strong U.V. absorption of both the tetramer and the polyTHF-pyridine species, a sample of high molecular weight polystyrene was added to the reaction mixture to act as an internal standard (trace (a) which

FIGURE 3.3.12.



MOLECULAR WEIGHT (POLYSTYRENE EQUIVALENT)

G.p.c. traces of (a) protonated monofunctional polystyrene used as u.v. standard and Grignard terminated α-methylstyrene tetramer, (b) methoxy terminated monofunctional polyTHF, (c) the product of the reaction between living polyTHF and Grignard terminated tetramer.

also shows the protonated tetramer). Trace (b) is of the pyridine-terminated monofunctional polyTHF and trace (c) is of the product of the reaction (equation 3.12.).

The relative areas of the tetramer and polystyrene after reaction (trace (c)) are about the same as initially (trace (a)) which indicates that very little addition has taken place. The system however, is undoubtedly more complicated than expected, since a red colour was generated by the reaction of the two components. Further experiments are necessary to elucidate the processes involved in the reaction.

From the g.p.c. curves shown in Figure 3.3.12. a measure of the degree of block copolymer formation was undertaken by the method outlined below.

Standard Solution: U.V. area of PS = 11.8, U.V. area of $\alpha_4^{=}$ = 4.3

Product Solution: U.V. area of PS = 4.9, U.V. area of $\alpha_4^{=}$ = 1.3

$$\text{Standard area ratio} = \frac{\alpha_4H_2}{PS} = 0.364$$

$$\text{Product area ratio:} = \frac{\alpha_4H_2}{PS} = 0.265$$

$$\text{Fraction of } \alpha_4H_2 \text{ remaining after reaction} = \frac{0.265}{0.364} = 0.73$$

and so the probability of proton transfer occurring can be measured

(see page 105);

$$P^2 = 0.73$$

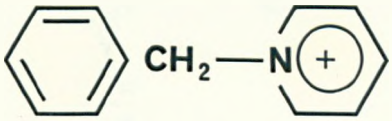
$$P = \underline{\underline{0.85}}$$

Therefore, approximately 15% of chains have formed block copolymer.

3.3. P.m.r. Analysis of Pyridine Terminated PolyTHF

A low molecular weight living polyTHF was terminated with pyridine and the product submitted for p.m.r. analysis.

Table 3.7. lists the assignments for the absorptions which were recorded in the p.m.r. spectrum (Figure 3.3.13.) of the pyridine-terminated polyTHF. It is clear the p.m.r. evidence supports the g.p.c. data that a stoichiometric reaction occurs between pyridine and polyTHF cations. There are traces of impurities present in the system as evinced by the small peaks at 5.8 δ, which is in the region of the spectrum which coincides with the methylene proton absorptions of adduct B.

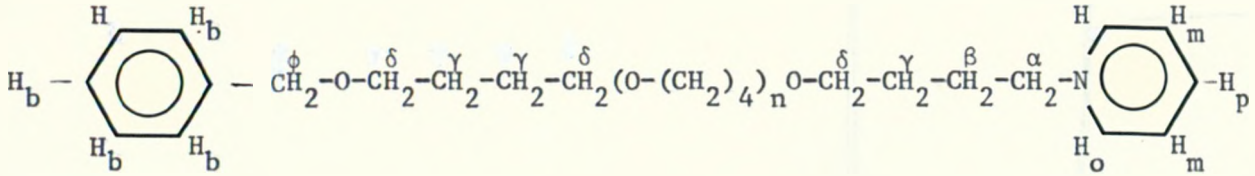


B

However, the proportion of this species present is insignificant compared with the desired product. Workers in Richards' laboratories at Waltham Abbey have repeated the p.m.r. study on pyridine-terminated polyTHF, as part of an investigation into the reactions of polymeric cations with tertiary amines, and have found no traces of adduct B spectroscopically. The formation of adduct B would only occur from reaction of unreacted benzyl bromide with pyridine, and since only minute traces are present (as evinced by the peak at 5.8 in the p.m.r. spectrum), reaction between benzyl bromide and silver hexafluorophosphate is rapid.

TABLE 3.7

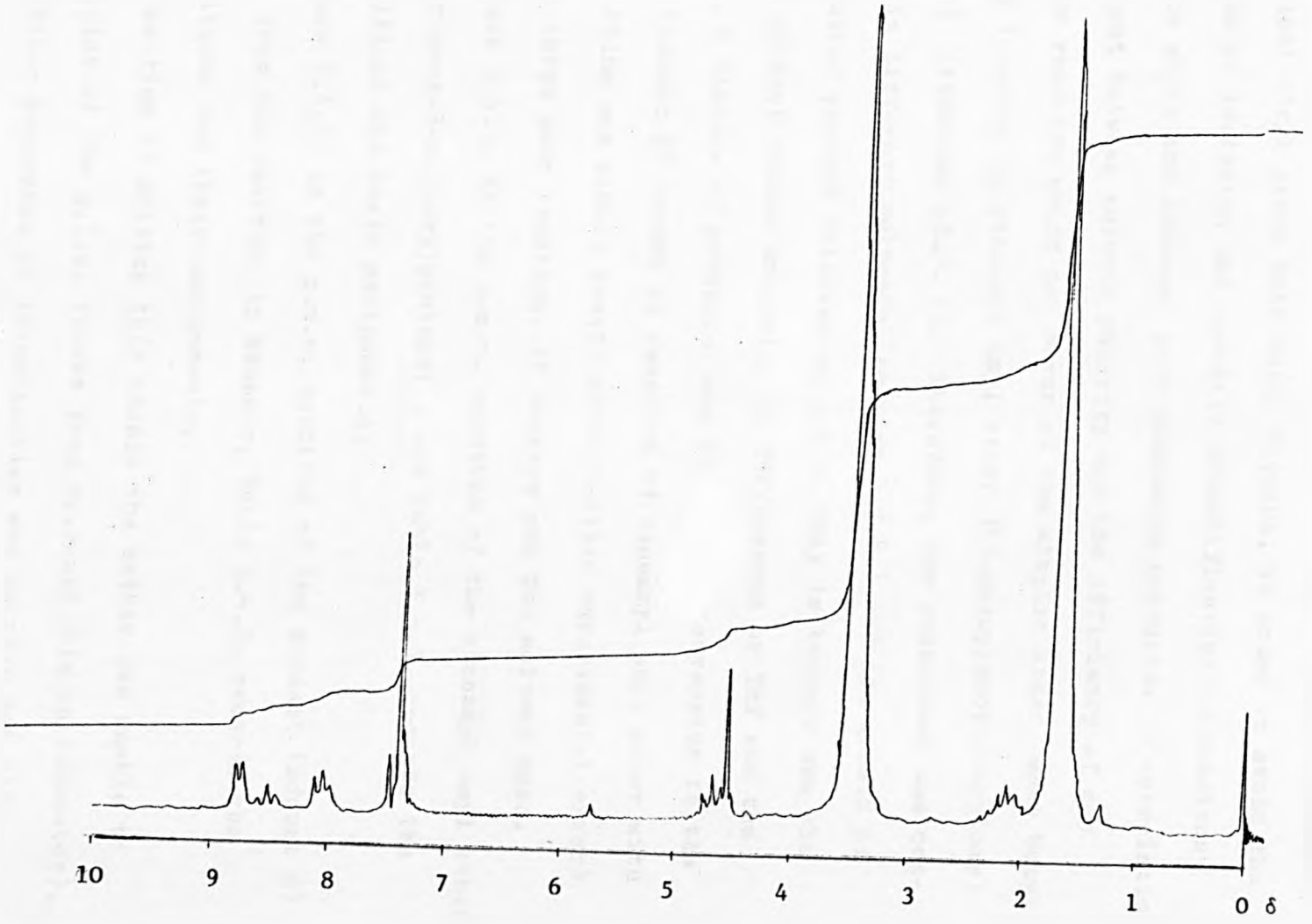
Assignment of the absorptions in the p.m.r. spectrum of pyridine-terminated polyTHF.



Peak Position (δ)	Assignment
8.8	H_o
8.5	H_p
8.1	H_m
7.5	$CHCl_3$
7.4	H_b
5.8	Methylene protons of adduct B.
4.7	α
4.6	φ
3.5	δ
2.1	β
1.7	γ

FIGURE 3.3.13.

A P.M.R. SPECTRUM OF A LOW MOLECULAR WEIGHT PYRIDINE TERMINATED POLYTHF.



3.4. Cationic to Anionic Transformation Process

The background to the present work on this transformation process has been recorded in section 1.6.3. Model compounds were used to investigate the reaction of polyTHF which possessed a terminal vinyl group with butyl lithium, in order to avoid the problems of isolation and specific indentification of reaction products which are inherent with polymeric products. A correlation was sought between solvent polarity and the efficiency of any cleavage reaction which may occur at the alkylic ether when butyl lithium is added to cinnamyl amyl ether [(3-phenylprop-2-enyloxy) pentane] (equation (2.7.)). Therefore, the experiment was conducted in different solvents (section 2.7.4.) and the growth of the required product followed by g.l.c. Only in benzene was the desired product formed uniquely, if THF/benzene or THF was the solvent, a mixture of products was obtained. Conversion to the product (adduct E) formed by reaction of cinnamyl amyl ether with butyl lithium was almost quantitative (within experimental error) during a three hour reaction, if benzene was the solvent used.

Figure 3.4.1. is the p.m.r. spectrum of the cinnamyl amyl ether [(3-phenylprop-2-enyloxy)pentane] , and Table 3.4.1. records the peak positions and their assignments.

Figure 3.4.2. is the p.m.r. spectrum of the product (adduct E) isolated from the reaction in benzene, Table 3.4.2. records the peak positions and their assignments.

At the time of writing this thesis the author was unable to obtain copies of the g.l.c. traces from Mr.Souel (his collaborator).

A similar programme of investigation was carried out with [(4-phenylbut-3-enyloxy)pentane] and n-butyl lithium. Tables 3.4.3.

FIGURE 3.4.1.

P.m.r. spectrum of cinnamyl amyl ether [(3-phenylprop-2-enyloxy)pentane].

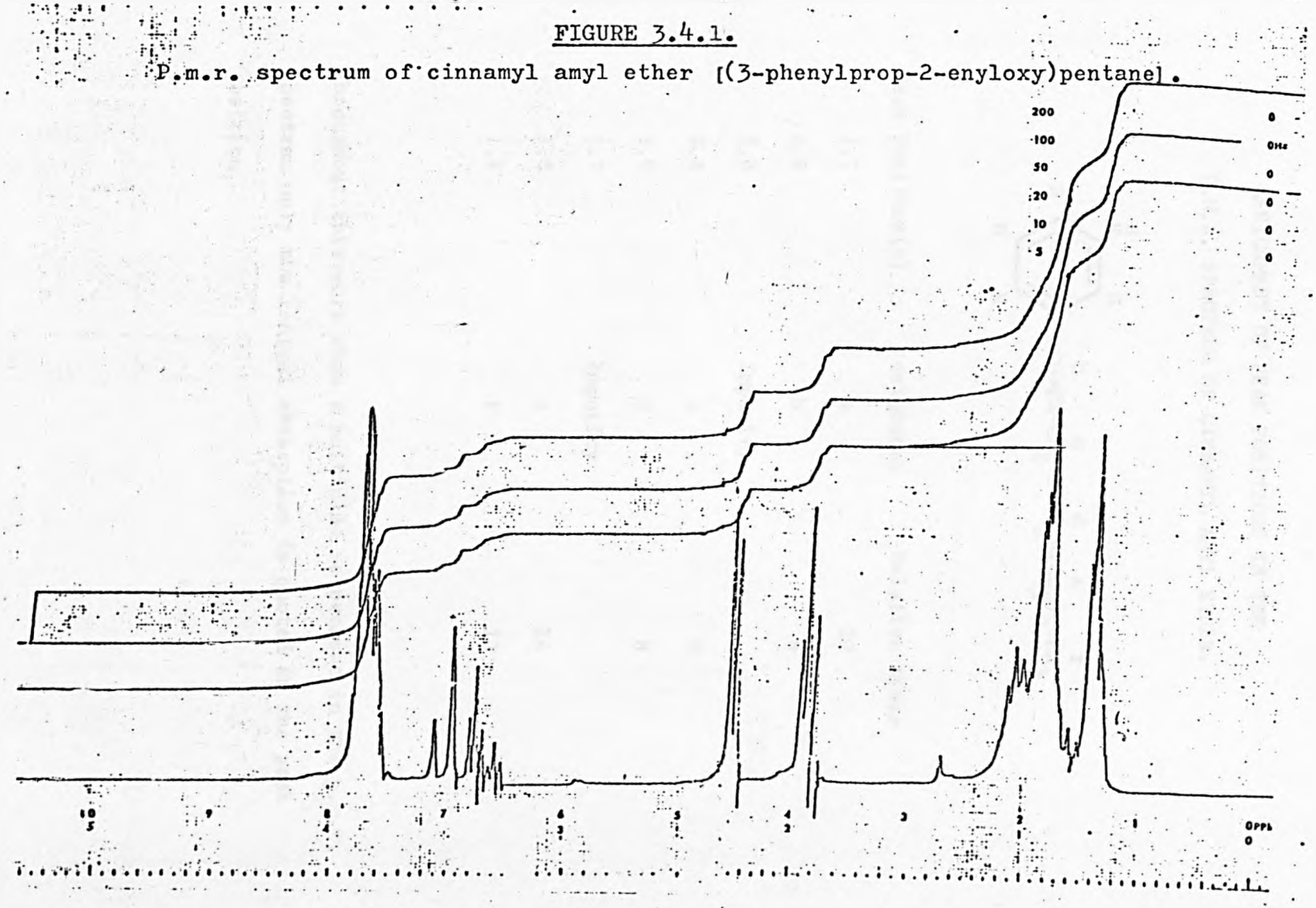
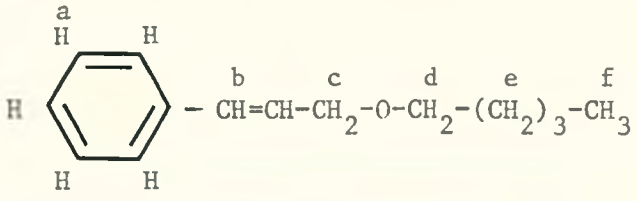


TABLE 3.4.1.

ASSIGNMENT OF PEAK POSITIONS IN THE

P.M.R. SPECTRUM OF CINNAMYL AMYL ETHER.



Peak Position(δ)	Assignment	Relative Areas
7.7	a	20
6.9	b	8
5.8	Impurity	
4.4	c	8
3.9	d	8
2.7	Impurity	
1.8	e	24
1.4	f	12

Throughout this work when a multiplet is present in the p.m.r. spectrum only the central absorption is quoted as the peak position.

FIGURE 3.4.2.

P.m.r. spectrum of the product obtained by reaction of n-butyl lithium with cinnamyl amyl ether [(3-phenylprop-2-enyloxy)pentane] in benzene.

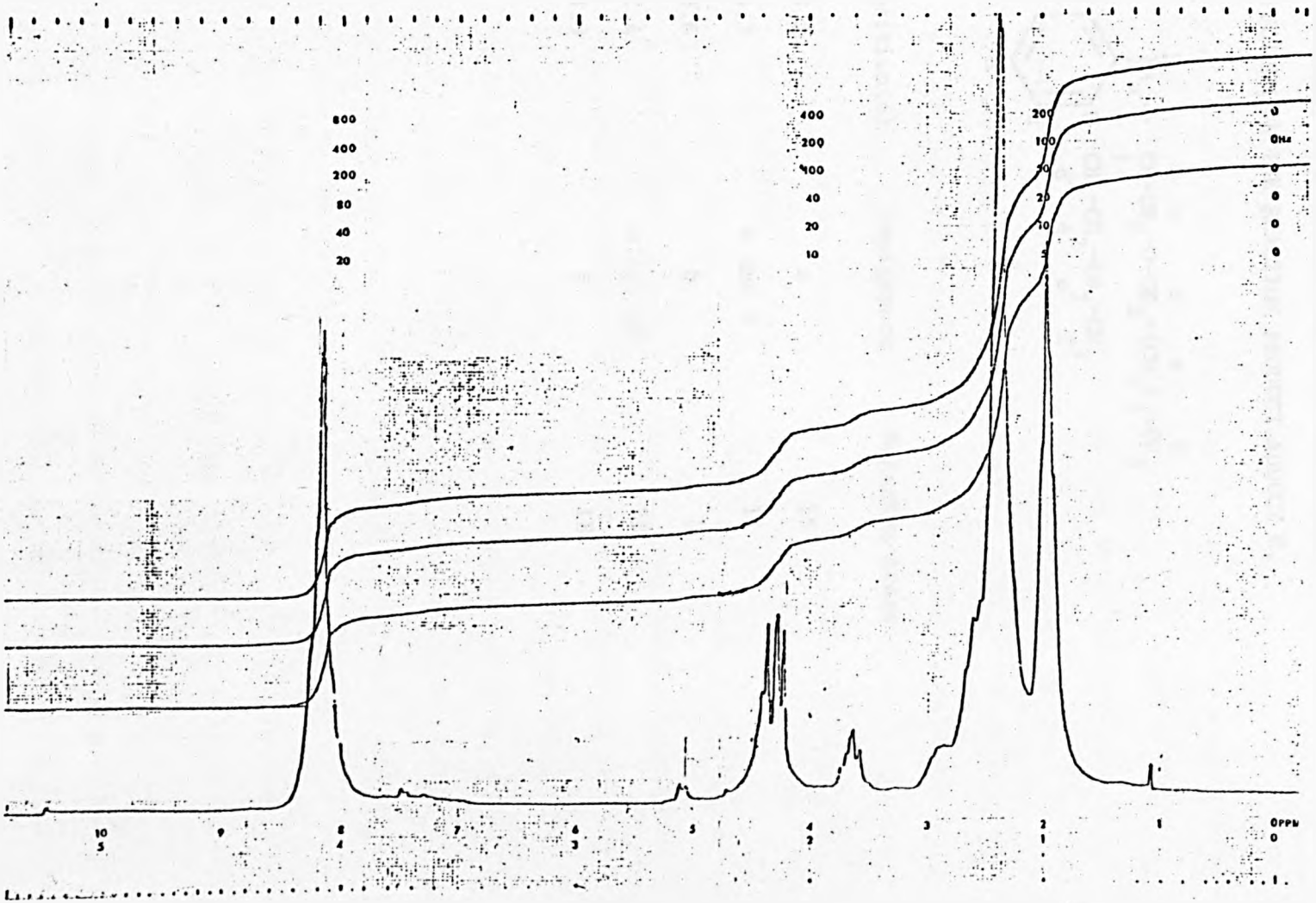
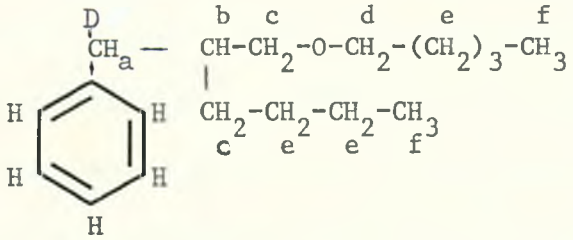


TABLE 3.4.2.

ASSIGNMENT OF PEAK POSITIONS IN THE P.M.R.

SPECTRUM OF THE REACTION PRODUCT ADDUCT E.



Peak Position(δ)	Assignment	Relative Areas
8.2	a	15
4.3	c and d	11
3.6	b	3
2.4	e	38
1.9	f	18

and 3.4.4. record the peak assignments in p.m.r. spectra of [(4-phenylbut-3-enyloxy)pentane] (Figure 3.4.3.) and the product (adduct F) (Figure 3.4.4.) which was obtained from reaction of the ether with butyl lithium in benzene for three hours.

From examination of the integration curves in the p.m.r. spectrum of adduct F(Figure 3.4.4.), it was calculated that after a three hour reaction in benzene 40% of the starting material remained. The reaction which occurs in benzene was still clean; whereas a mixture of products was obtained in the other solvent systems. Therefore, the [(4-phenylbut-3-enyloxy)pentane] was no longer considered to be useful to the investigation because of this incomplete addition of n-butyl lithium (within the three hour reaction period) compared to the cinnamyl amyl ether.

The p.m.r. data obtained showed that addition (equation(1.2 4)) rather than cleavage (equation(1.2 5)) was occurring. An experiment was performed in which a living polyTHF was prepared as described in section 2.3.5. and terminated with cinnamyl alkoxide. The solvents, THF from the polymerisation and THF/benzene from the cinnamyl alkoxide preparation were removed. The polymer was redissolved in benzene and butyl lithium added. Unfortunately, the red colour disappeared, although more slowly than in the presence of THF. Termination of the styryl anion was still occurring and so attention was directed to the possibility of cleavage at the initiation site of THF polymerisation i.e. cleavage of the benzylic ether. To investigate this possibility the model compound benzyl butyl ether was prepared as outlined in section 2.7.6., and was reacted with n-butyl lithium (section 2.7.7.) in the different solvent systems. These reactions were followed by g.l.c. In benzene no cleavage of the ether was

FIGURE 3.4.3.

P.m.r. spectrum of [(4-phenylbut-3-enyloxy)pentane].

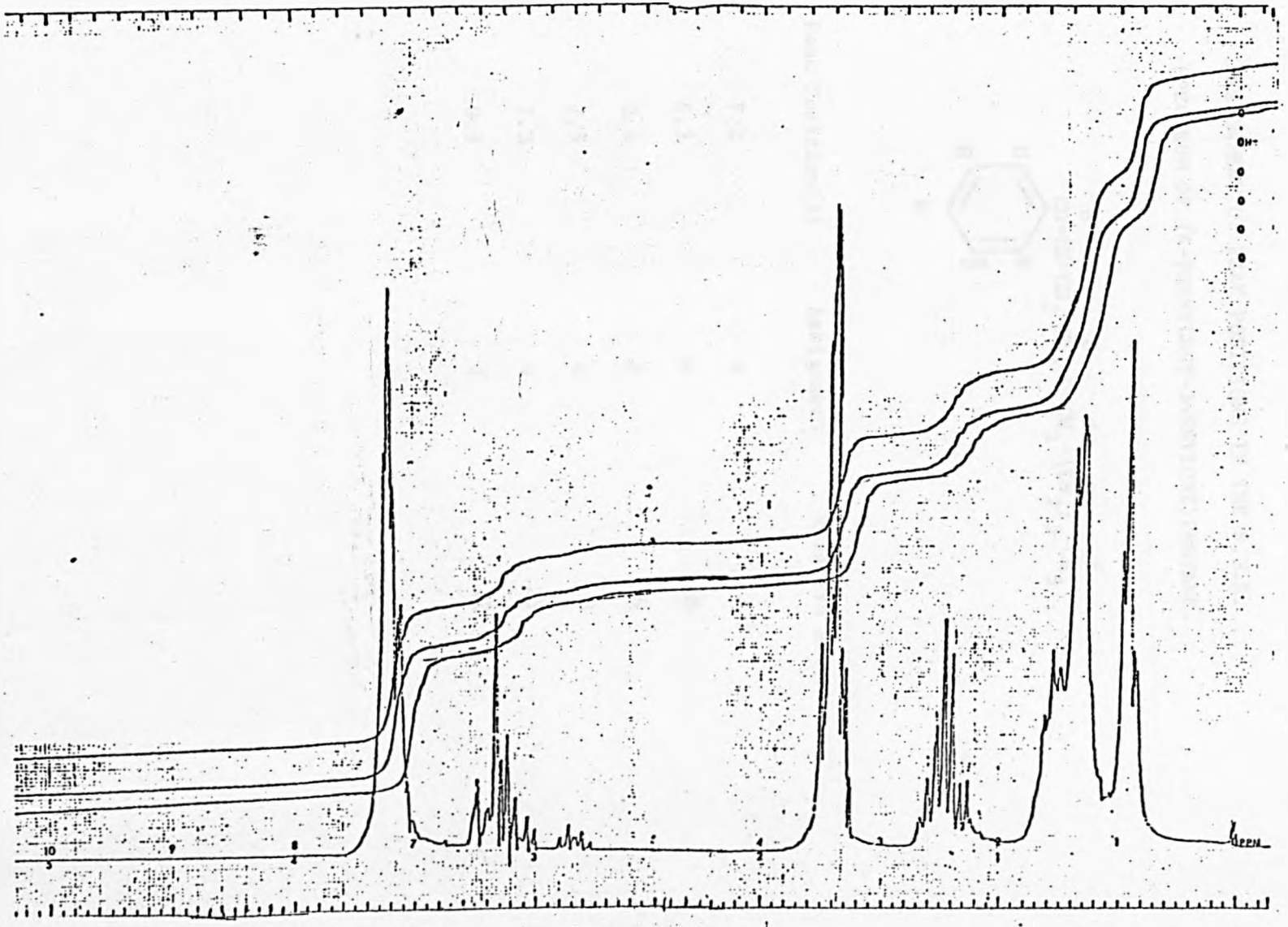
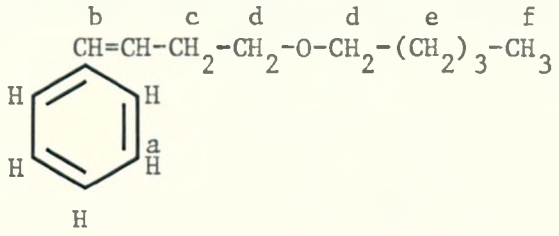


TABLE 3.4.3.

ASSIGNMENT OF PEAK POSITIONS IN THE P.M.R.

SPECTRUM OF (4-PHENYLBUT-3-ENYLOXY)PENTANE.



Peak Position(δ)	Assignment	Relative Areas
7.2	a	2.1
6.3	b	8
3.4	d	16
2.5	c	8
1.3	e	25
0.9	f	12

FIGURE 3.4.4.

P.m.r. spectrum of the product obtained by reaction of n-butyl lithium with [(4-phenylbut-3-enyloxy)pentane].

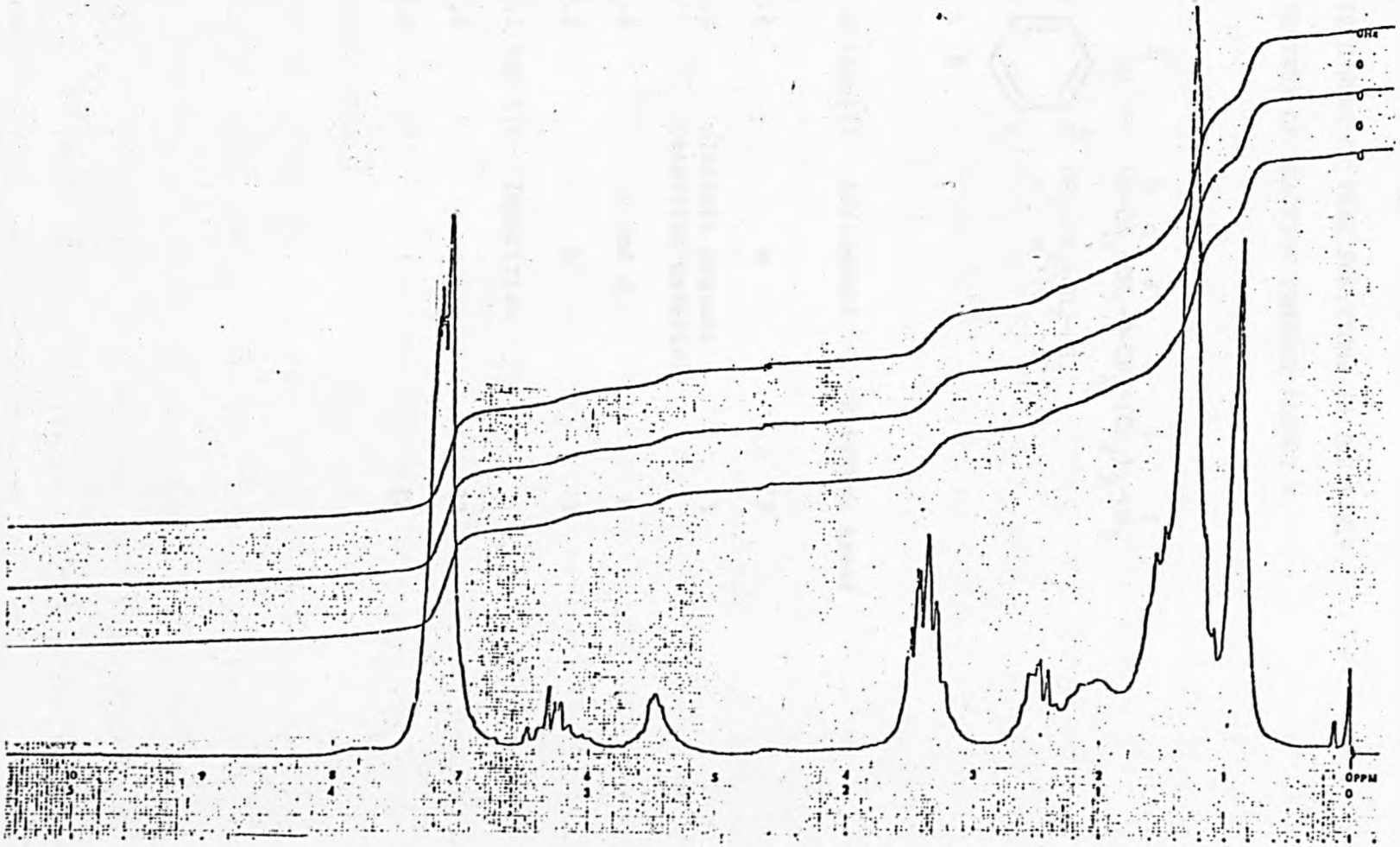
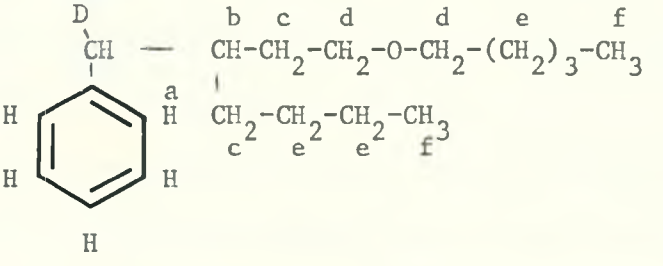


TABLE 3.4.4.

ASSIGNMENT OF PEAK POSITIONS IN THE P.M.R.

SPECTRUM OF REACTION PRODUCT ADDUCT F.



Peak Position(δ)	Assignment	Relative Areas
7.1	a	15
6.3	olefinic protons (starting material)	3
3.4	c and d	6
2.5	b	3
2.1 and 5.6	Impurities	
1.4	e	33
0.9	f	11

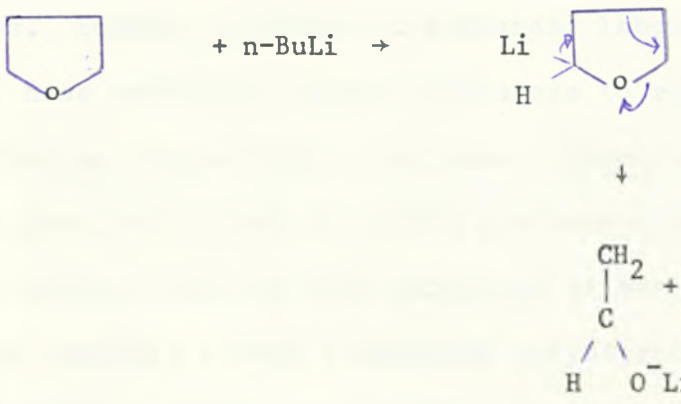
seen after a three hour reaction. When THF was present in the solvent many peaks appeared on the g.l.c. trace. However a similar trace was observed when a THF solution of butyl lithium was allowed to stand for three hours. Butyl lithium is known[78] to react directly with THF via pathways such as that shown in equation (3.13.), and this complication could account for the complexity of the g.l.c. traces obtained from the butyl lithium, benzyl butyl ether, THF system. The unsuitability of THF as a solvent for these reactions is, however, demonstrated clearly when an equimolar mixture of the benzyl butyl ether and cinnamyl amyl ether was reacted with butyl lithium in benzene (section 2.7.8.) for three hours. The products were found to be unreacted starting materials, and the adduct G. These facts suggest that the reaction had not reached completion. However, this experiment was conducted once and should be repeated to check the results. Isoprene was then used instead of styrene (equation (1.24.)) in the reaction with cinnamyl-terminated polyTHF in benzene. G.p.c. traces of the product have revealed that approximately 40% block copolymer was formed.

Because the author was concerned more with the model compound investigation as part of the cationic to anionic transformation study, comments will be limited to this work.

It might be postulated, that the fading of the red colour of the polystyryl anion with time was due to traces of impurities in the system. However, this seems unlikely since equally delicate reactions have been performed under nitrogen with the retention of colour. Nevertheless for future work it is planned to use vacuum conditions (see Suggestions for Further Work, section 3.6.).

From the results obtained to date certain tentative assessments can be made. Firstly, the model compound experiments have proved

that the anionic initiator can be generated in quantitative yield when benzene is the solvent. Secondly, in this solvent there is no cleavage at the benzyl ether linkage. The reaction of the equimolar mixture of benzyl butyl ether and cinnamyl amyl ether with butyl lithium is not understood fully and should be repeated although, again, no attack on the benzyl ether linkage was observed. Finally, the preliminary study with polymeric systems has indicated that the transformation process is complex but further experimentation with model compounds has indicated that under well defined conditions, block copolymers should be formed.



(3.13.)

3.5. Conclusions

The work on the block copolymerisations with polymeric anions and cations involved two separate areas of study: (1) the efficient preparation of living polymers and (2) the titration of the polymeric cations with polymeric anions to provide a convenient pathway to block copolymers.

The first area of study was successful, since polymers of narrow molecular weight dispersities were prepared easily. The results obtained from the second area of investigation were extremely interesting. Very high linking efficiencies of polystyrene anions with living polyTHF have illustrated that the titration technique is an efficient method for preparing block copolymers of these two species. However, workers in Richards' laboratories at Waltham Abbey, have failed on several occasions to reproduce these results: On titration of the living polymers a black colouration was obtained. It has been postulated that this phenomenon results from the polystyryl anions reacting with unreacted silver hexafluorophosphate to form an unstable silver terminated polystyrene which decomposes to silver metal and polystyrene radicals. An investigation to determine the source of this problem has commenced. Only limited block copolymerisation was achieved with living poly(α-methylstyrene) and living polyTHF and the α-methylstyrene tetramer dianion with living polyTHF, and virtually no linking was achieved with polymers having a terminal 1,1-diphenylethylene anion and living polyTHF.

Transformation of the living polymer into the Grignard derivative increased slightly the efficiency of linking, but alternative routes still have to be found to produce polyTHF-poly(α-methylstyrene) block copolymers efficiently.

The reactions involving pyridine were possibly of the greatest significance since they have potentially far-reaching analytical

and synthetic applications. This would be particularly so if the process were of applicability to tertiary amines in general, since mono and diamines could be employed to prepare block copolymers of a variety of different structures.

The work reported in this section of the thesis was conducted under nitrogen rather than under the more stringent high vacuum conditions. Although the accuracy of the work must necessarily suffer from using the former system, it is however closer to the conditions employed for industrial processes, so that positive results obtained in these circumstances can have very real commercial significance if the cost is right.

3.6. Suggestions for Further Work

(a) The quantitative linking achieved by reacting living anionic polystyrene with living polyTHF indicates that this method could be used to prepare AB, ABA, BAB and $(AB)_n$ block copolymers from these materials very specifically. This process should be developed to produce such materials so that morphological studies on them can be performed.

(b) The efficiency of the linking reaction of living polyTHF with anionic polydienes is currently being examined. If this should also be quantitative, then block copolymers involving these materials can also be prepared. Further, by initially preparing anionic AB poly (styrene-b-butadiene), ABC, ABCBA block copolymers can be produced. Permutation on this theme by preparing di- anionic ABA poly(styrene-b-butadiene) would also enable CABAC, and $(ABC)_n$ block polymers to be prepared and studied.

(c) The reaction between living polyTHF and 1,1-diphenylethylene terminated polymeric anions should be checked to ensure that the indications of no linking observed in the present investigation are substantiated.

(d) A detailed study should be made of the reaction between anionic poly(α-methylstyrene) and pyridine terminated polyTHF, to determine the nature of the reactions involved.

(e) The reaction of n-butyl lithium with the equimolar mixture of cinnamyl amyl ether and benzyl butyl ether should be repeated to confirm the present result. Since the experiment was performed only once it is necessary to validate the findings by repetition.

(f) Attention should be directed towards the copolymerisation studies with cinnamyl terminated polyTHF; the THF solvent must be replaced by benzene before addition of n-butyl lithium and subsequent reaction with monomer.

Ethylene oxide should be tried as second monomer in this system; addition of the first monomer unit should be signalled by the elimination of the characteristic red styryl colour, and the homopolymerisation of this monomer is smooth and has been well documented[79].

These studies should be repeated under high vacuum conditions, so that comparison may be made with the results obtained under nitrogen. High vacuum techniques are more rigorous, resulting in less impurities which are capable of side reactions.

References to CHAPTER 3.

73. F.J. Burgess, A.V. Cunliffe, J.V. Dawkins and D.H. Richards, Polymer, 1977, 18, 733.

74. F.J. Burgess, A.V. Cunliffe, J.R. MacCallum and D.H. Richards, Polymer, 1977, 18, 726.

75. D.H. Richards and N.F. Scilly, J. Chem. Soc., (C), 1969, 55.

76. A. Davis, M.H. Morgan, D.H. Richards and N.F. Scilly, J. Chem. Soc., (Perkin), 1972, 286.

77. T. Saegusa, S. Matsumoto and Y. Hashimoto, Polymer, 1970, 1, 31.

78. B.J. Wakefield, "The Chemistry of Organolithium Compounds", Pergamon Press, Oxford, 1974.

79. N.G. Gaylord, "High Polymers", XIII, (1), Interscience, LONDON, 1963.

PART B

SULPHUR WORK

CHAPTER 4

INTRODUCTION

4.1. Background Study

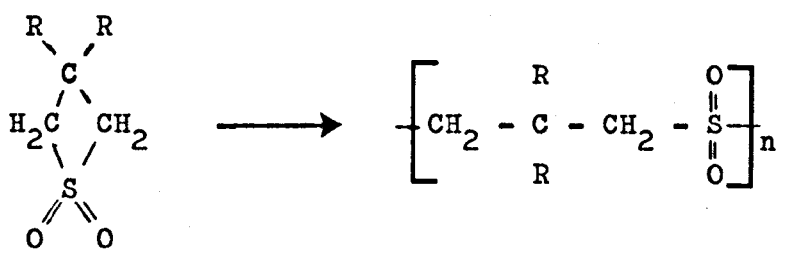
This work is concerned with the susceptibility of cyclic sulphones to ionic and free radical attack and subsequent polymerisation. The polymerisability of these compounds by a ring opening mechanism should be related to the ring strain in the monomer, and therefore differences should be observed between the reactivities of 3,4 and 5 membered rings in particular. Unfortunately, time restrictions required that only a limited examination of these systems could be undertaken, and the work reported in this thesis is confined to a study of the susceptibilities of 4 and 5 membered cyclic sulphones towards nucleophilic, electrophilic and free radical attack.

The class of compounds which contain the sulphonyl group $-\overset{O}{\underset{O}{S}}-$ attached directly to two carbon atoms, either in cyclic or linear structures, are termed sulphones[1]. Their interesting chemical and physical properties have been exploited in many areas of polymer[2], heterocyclic[3] and synthetic organic chemistry[4]. The present study is connected with the role of sulphones in polymer chemistry.

Polysulphones have gained technological importance, finding use mainly as specialised thermoplastics[5]. Good heat-deflection properties and very low creep rates permit aromatic polysulphones to be employed as useful engineering materials[6]. For example, a polyarylsulphone can retain good tensile and compressive strength at 533K for extended periods and large research programmes have been carried out over a number of years on the production of polysulphones from aromatic sulphone monomers[7,8]. Aliphatic polysulphones have received less attention (as evinced by the literature available) and very little information is available about their direct preparation from aliphatic sulphone monomers. The reasons for the lack of interest lie in the thermal and hydrolytic instability of the early aliphatic

polysulphones which were formed from reaction between olefins and sulphur dioxide. Although high melting, these poly-2,3-sulphones show catastrophic failure at elevated temperatures, and this instability has been related to the fact that a primary chain scission at a C-S bond can result in facile regeneration of the component monomers by an unzipping mechanism. However, polysulphones possessing at least four methylene units between sulphonyl groups are thermally and hydrolitically stable[9].

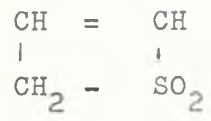
On this basis poly(3,3-dialkyl trimethylene sulphone) materials should exhibit attractive properties since they should be high melting because of the high concentration of sulphone groups coupled with the stiffening effects of the pendent alkyl groups, and thermally stable because they are incapable of facile unzipping after primary scission to produce an olefin and sulphur. In theory these materials may be prepared by a ring opening polymerisation of the parent thietan dioxide (equation (4.1)) and it was planned to prepare such polymers by this means.



(4.1)

Unfortunately, a literature survey showed that attempts to homopolymerise these monomers had failed and so it was considered necessary to enhance the susceptibility of the thietan ring to electrophilic attack at the C-2 or C-4 position. It seemed that this could have been done by incorporating electron-donating substituents at the C-3 position, and conversely, electron-withdrawing substituents at this

(1)



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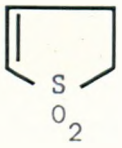

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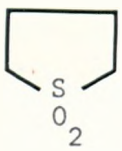
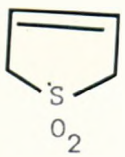


(4)



position for nucleophilic attack. Several such compounds were therefore prepared and tested for their polymerisability by ionic and free radical initiators.

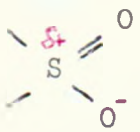
The polymerisation of four-membered unsaturated cyclic sulphones has not been reported. Therefore, attempts to polymerise thiete-1,1-dioxide (1) by reaction with anionic, cationic and free radical initiators were tried.

There is little literature on the polymerisation of five-membered cyclic sulphones. Geothals[11] reported that 2-sulpholene (2) may be copolymerised with vinyl acetate by a free radical mechanism but not homopolymerised by any mechanism. Sulpholane (3) and 3-sulpholene (4) were studied by the author (Kingston)

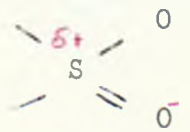
as possible components for a specially devised copolymerisation process (section 5.6.3.). Rather than attempt a general review of each class of cyclic sulphone studied it was considered to be more relevant to record those aspects important to the present investigation.

4.2. Review of Thietan-1,1-Dioxide Chemistry

Like the linear sulphones, the four-membered cyclic sulphones are chemically quite stable[12]. Their stability resides in the sulphonyl group which has been shown to be most heavily populated in the canonical forms (A) and (B)[13].

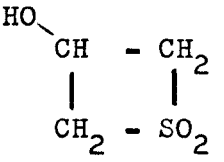


(A)

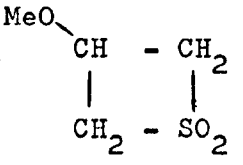


(B)

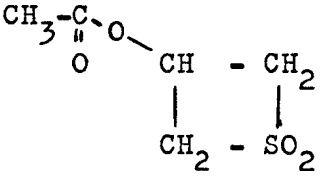
(5) 3-thietanol-1,1-dioxide



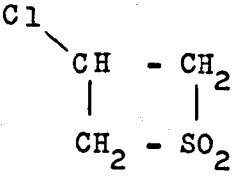
(6) 3-methoxythietan-1,1-dioxide



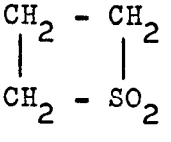
(7) 3-acetoxythietan-1,1-dioxide



(8) 3-chlorothietan-1,1-dioxide



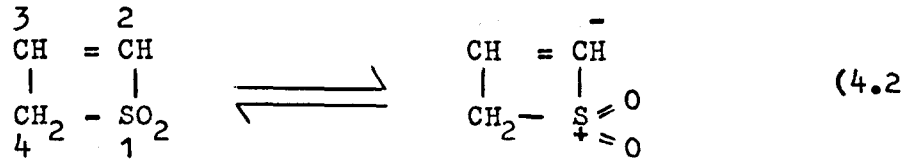
(9) Thietan-1,1-dioxide



Through the absence of reactive double bonds, the sulphonyl group is virtually devoid of any reactivity and reduction occurs only with great difficulty[4]. Thus the chemical reactivity of the sulphones depends in general on the reactivity of the carbon-sulphur bond. Formally, there are three possible ways in which the C-S bond may be broken: Heterolytically, where the sulphur atom retains both bonding electrons or retains neither; or homolytically, where the electrons are shared. These routes would result in an anionic, cationic or free radical sulphur respectively and, as might be expected from the relative electronegativities of sulphur and carbon, heterolytic cleavage to yield a negatively charged sulphur is by far the most common. Therefore to promote cleavage of the C-S bond required for a ring-opening polymerisation, electron-donating substituents were introduced at the C-3 position. The following four-membered cyclic sulphones were therefore prepared. 3-Thietanol-1,1-dioxide (5), 3-methoxythietan-1,1-dioxide (6), 3-acetoxythietan-1,1-dioxide (7), 3-chlorothietan-1,1-dioxide (8). There is no record of any attempts to polymerise these compounds. However, thietan - 1,1-dioxide (9) was found to be unpolymerisable by Etienne et al.[14].

4.3. Review of Thiete-1,1-Dioxide Chemistry

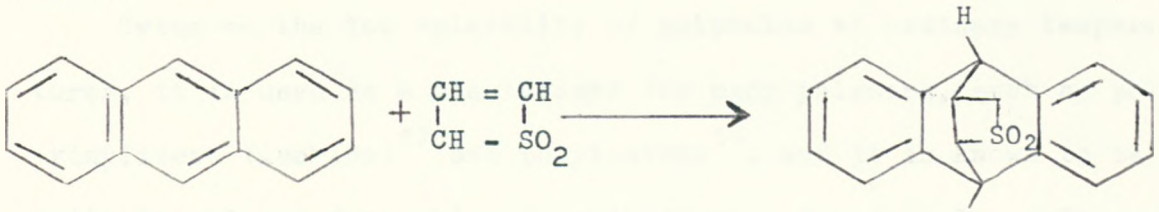
The structure of thiete-1,1-dioxide has been confirmed by nuclear magnetic resonance measurements[4]. The electron density on C-3 seems to be less than that on C-2, which suggests a displacement of electrons according to the following equation (4.2.)



(4.2)

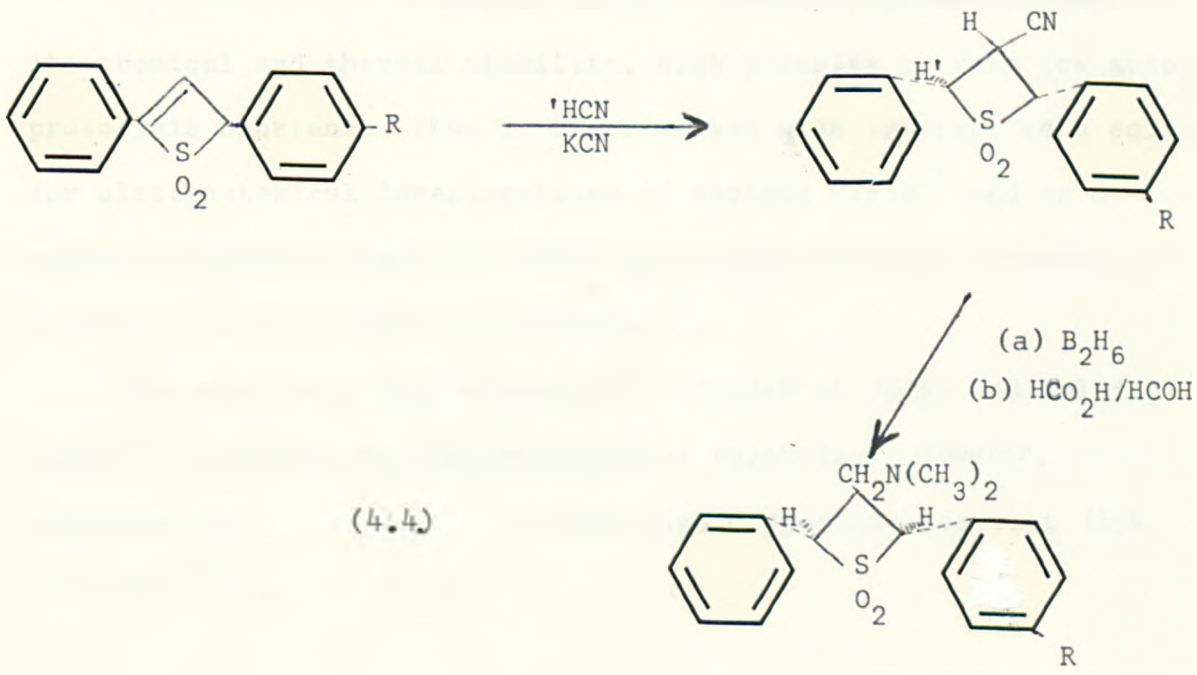
Thiete-1,1-dioxide exhibited no absorption in the ultraviolet between 220-420nm at a concentration of 10^{-3}M in alcohol. Its infra-red spectrum[4] has vibrational frequencies at 3165 cm^{-1} (C-H), 1543 cm^{-1} (C=C), 1136 and 1290 cm^{-1} (S=O) and 697 cm^{-1} (C-S). These values are in good agreement with those determined in the present work section 6.1.

Reaction of thiete-1,1-dioxide and anthracene in toluene, in a sealed tube at 420K formed the Diels-Alder adduct[14](C),(equation (4.3.)).



(4.3.) (C)

Substituted thiete-1,1-dioxides have been used in the syntheses of novel compounds[15], (equation (4.4.)).



(4.4)

4.4. Review of Sulpholan and Sulpholene Chemistry

In recent years the interest in sulpholan (the trivial name of tetrahydrothiophene-1,1-dioxide or tetramethylene sulphone) has encompassed both applied and pure chemistry.

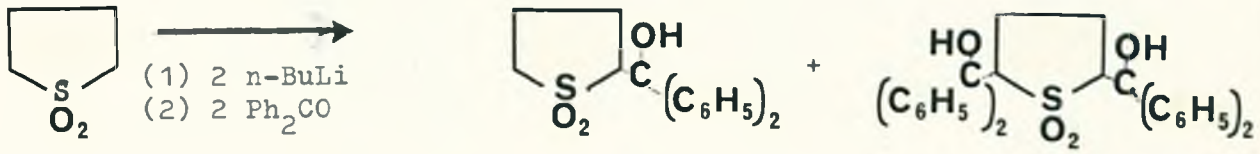
In applied chemistry, sulpholan is known as an important technical solvent for many extraction processes[16]. In the petrochemical industry it is useful because of its ability to extract selectively aromatic from aliphatic hydrocarbons and to absorb waste gases.

Owing to the low volatility of sulpholan at ordinary temperatures, it is used as a plasticizer for many polymers, such as poly(vinylidene fluoride)[17] and polylactams[18], and it is known to be a suitable solvent from which to spin fibres; for example, polyacrylonitrile fibres have been produced in this way[19]. Sulpholan has also found use in the preparation of permeable membranes from cellulose acetate[20], in the preparation of photographic emulsions[21,22], and in the preparation of metallized films and fibres[23].

Applications of sulpholan in pure chemistry primarily exploit its chemical and thermal stability, high polarity or very low autoprotolysis constant. Thus it has received wide interest as a solvent for electrochemical investigations of various kinds[24] and as a medium in which to carry out many reactions which are affected by solvent of a more reactive character[25].

The relatively high viscosity[26] (10.3cP at 303K) and melting point[27] (301.45K) are disadvantages of sulpholan. However, sulpholan has a very high cryoscopic constant (65K $g\ mol^{-1}$)[27].

Sulpholan is a good aprotic solvent, dissolving molecular and ionic substances[28] without being attacked by even such strongly electrophilic species as the nitronium ion[29]. It also forms a 1:1 complex with borontrifluoride[30] but reacts with strong nucleophiles to generate carbanions[31]. The treatment of sulpholan with two equivalents of n-butyl lithium followed by two equivalents of benzophenone afforded an 80% yield of di-adduct (II)and 18% of mono-adduct (III) (equation (4.5)).



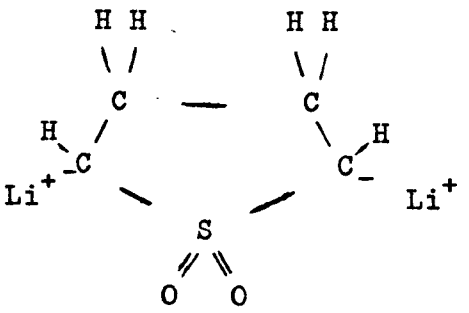
(III)
18%

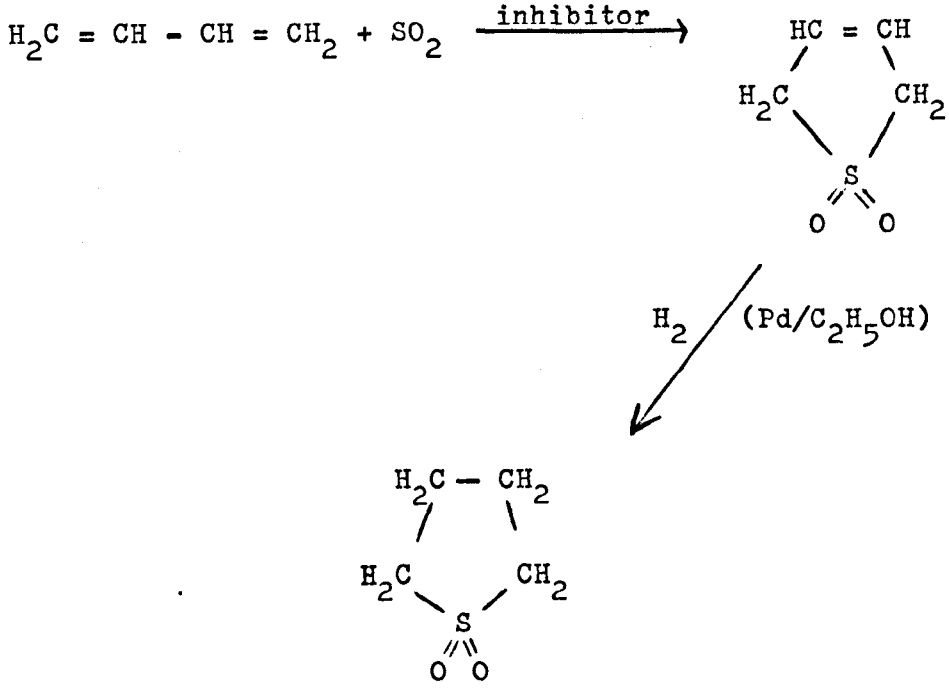
(II)
80%

(4.5.)

Hauser[32] has reported that treatment of sulpholan with two moles of lithium amide followed by benzophenone produced only monoadduct, while use of sodium amide resulted in a 41% yield of (III) and a 48% yield of (II). In the present work a preparative route with butyl lithium was used to prepare a series of copolymeric and low molecular weight compounds, and these were characterized by p.m.r., infra-red etc. 3-Sulpholene (also called butadiene sulphone, 2-5, dihydrothiophene-1,1-dioxide) is obtained easily by reaction of butadiene with sulphur dioxide in the presence of polymerisation inhibitors[33] and is made in large quantities as an intermediate in the manufacture of sulpholane[33], (equation (4.6)).

(10)





(4.6)

Since all attempts to homopolymerise 3-sulpholene have failed[11], and efforts to copolymerise it were also unsuccessful[11], so any synthetic pathway which succeeded in incorporating the species in a polymer chain would be novel. Use of n-butyl lithium to generate from sulpholan the α,α' dianion (10) which would then be reacted with other difunctional species to produce copolymers was thought to be feasible. Part B of this thesis is the experimentation which involves 3-sulpholene and sulpholane, together with the syntheses and polymerisation testing of the four-membered cyclic sulphones.

4.5. Thietan-1-Oxide

For a brief insight into the polymerisability of the four-membered cyclic sulphoxides thietan-1-oxide was prepared and tested with butyl lithium. Due to time limitations no further experiments were carried out with other initiators or with other cyclic sulphoxides.

References to CHAPTER 4.

1. M.R.F. Ashworth, "The Determination of Sulphur-containing Groups", Academic Press, London and New York, 1972.
2. K.J. Ivin and J.B. Rose, Adv. in Macromol. Chem., 1968, 1, 335.
3. L. Paquette and M. Rosen, J. Org. Chem., 1968, 33, 3027.
4. D.C. Dittmer and M.E. Christy, J. Org. Chem., 1961, 26, (4), 1324.
5. R.K. Walton, "Modern Plastics Encyclopaedia", 1969-1970.
6. R.K. Walton, "Modern Plastics Encyclopaedia", 1970-1971.
7. A. Kreuchunas, U.S. Patent 2822351, 1958.
8. W.R. Sorenson and T.W. Campbell, "Preparative Methods of Polymer Chemistry", Interscience, New York, (2nd Ed.), 1968.
9. H.D. Noether, Text. Res. J., 1958, 28, 533.
10. V.S. Foldi and W. Sweeny, Makromol. Chem., 1964, 72, 208.
11. E.J. Goethals, Makromol. Chem., 1967, 109, 132.
12. G. Opitz and H. Adolph, Angew. Chem. internat. Edit., 1962, 1, 113.
13. A. Kolesnik and V.V. Kozlov, Russ. Chem. Revs., 1968, 37, (7), 519.
14. Y. Etienne and R. Soulas, "Heterocyclic Compounds", 1964, 2, 707, Interscience.
15. J.E. Coates and F.S. Abbot, J. Org. Chem., 1977, 42, (22), 3506.
16. G.S. Morrow, Encycl. Chem. Technol., 1969, 19, 250.
17. D,R. Seibel and F.P. McCandless, Ind, Eng. Chem., 1974, 13, 76.
18. W.E. Garrison and T.J. Hyde, U.S. Patent 3,361,697, 1968.

19. P.M.P. Eller, Diss. Abstr. Int. B, 1972 33, 2976.

20. W.E. Skiens, German Patent 1,923,187, 1970.

21. Gevaert-Agfa N.V., Neth. Patent Appl., 6,516,423, 1966.

22. K.J. Jacobson, British Patent 1,038,029, 1966.

23. J. Patschorke, German Patent 2,022,109, 1971.

24. N.R. Armstrong, R.K. Quinn and N.E. Vanderborgh, Anal. Chem., 1974, 46, 1759.

25. W.R. Fitzgerald, A.J. Parker and D.W. Watts, J. Amer. Chem. Soc., 1968, 90, 5744.

26. L. Jannelli and A. Sacco, J. Chem. Thermodyn., 1972, 4, 715.

27. M. Della Monica, L. Jannelli and U. Lamanna, J. Phys. Chem., 1968, 72, 1068.

28. R.S. Drago in "Non-Aqueous Solvent Systems", T.C. Waddington, Ed., Academic Press Inc., New York, 1965.

29. J. Jones and J. Jones, Tetrahedron Letters, 1964, 31, 2117.

30. W.E. Truce and T.C. Klingler, J. Org. Chem., 1970, 35, 1834.

31. C.R. Hauser and E.M. Kaiser, Tetrahedron Letters, 1967, 3341.

32. Y. Minoura and S. Nakajima, J. Polym. Sci., Part A-1. 1966, 4, 2929.

CHAPTER 5

EXPERIMENTAL

5.1. Materials

(a) Solvents

In this study g.l.c. was used to check the purity of the solvents and reagents.

Tetrahydrofuran and Analar benzene (B.D.H. Ltd.) were purified by the method reported in section 2.1. of this thesis. Only the middle fractions were collected at 339K (760 mm Hg) for THF(Lit.[34] 338 - 340K at 760mm Hg), and at 354K (760mm Hg) for benzene (Lit.[34] 353.2K at 760mm Hg).

Analar nitrobenzene (B.D.H. Ltd.) used for the polymerisation tests was vacuum distilled, the middle fraction was collected at 383.5K (0.1mm Hg) (Lit.[34] 483-485K, at 760mm Hg) and this was recrystallised twice from itself.

Pyridine and s-collidine (Aldrich Chemical Co. Ltd.) were dried by refluxing them with sodium hydroxide pellets, and fractionally distilling, collecting the middle fractions; at 398K (760mm Hg) for pyridine, (Lit.[34] 388K at 760mm Hg), and 444K (760mm Hg) for s-collidine (Lit.[34] 444-445K at 760mm Hg).

Methanol and Hexane (B.D.H. Ltd.) were used for precipitating the polymers and received no purification.

Dichloromethane (Fisons Chemicals Ltd.) was purified as described by Perrin et al.[35] The solvent was then refluxed over calcium hydride for several hours and fractionated in a Normatron automatic laboratory distillation apparatus with a reflux ratio of at least 25:1. The middle fraction was collected at 313K (760mm Hg) (Lit.[35] 312.95K at 760mm Hg) and stored in dark Winchester bottles.

(b) Initiators

n-Butyl lithium (Koch-Light Ltd.) was purchased as a 1.6M solution in hexane and was stored in a refrigerator at 258K. Contact with the air was minimized.

n-Butyl lithium (in THF) was prepared as follows in the apparatus shown in Figure 2.3. Lithium (14g, 2 mole) strips were added to THF (350ml) in a round-bottomed flask (500ml), H, fitted with a nitrogen inlet, suba-seal, alcohol thermometer and a transfer tube (to which a filter-bulb of porosity 3 was attached) leading to an empty round-bottomed flask (500ml), G, fitted with a nitrogen inlet and suba seal.

n-Butyl bromide (64.5ml, 0.6 mole) was added dropwise from a syringe into the gently stirred, cooled (243K) lithium/THF mixture in approximately 45 minutes. Once the addition had been completed, the reaction mixture was kept at 243K for 2 hours. Then a 2ml sample was withdrawn and tested with styrene for the characteristic cherry red colour of the styryl anion.

The 1M solution of n-butyl lithium in THF was filtered into the empty flask (G) via the transfer tube by nitrogen pressure.

A Gilman titration[36] was carried out on the filtered solution to obtain the exact concentration.

Lithium fluorenyl was prepared by Morton and Fetters' method.[37]

Boron trifluoride etherate (B.D.H. Ltd.) was used as supplied.

Perchloric acid was prepared by former workers in these laboratories and stored in phials; these phials were used in experiments conducted under nitrogen.

Trifluoroacetic acid (Koch-Light Ltd.) phials containing the purified acid were prepared by Dr. W. Obrecht in this laboratory and used by the author.

Benzoyl peroxide (B.D.H. Ltd.) was used as supplied.

Titanium tetrachloride in carbon tetrachloride was used from a stock solution available in the laboratory. Care was exercised to ensure that the supply remained completely colourless, by removing aliquots with a syringe under a nitrogen blanket.

Stannic chloride (Koch-Light Ltd.) was used without purification, contact with the air being minimized by observing the precautions followed with titanium tetrachloride.

Sodium naphthalene (in THF) was prepared as described in section 2.3.2.

(c) Reagents

3-Thietanol (Robinson Brothers Ltd.) was purified by two distillations under vacuum in which only the middle fractions were collected at 353K (10mm Hg) (Lit.[38] 335K at 2mm Hg).

Sulpholan (Koch-Light Ltd.) was vacuum distilled from sodium hydroxide pellets, the middle fraction was collected at 463K (0.1mm Hg) (Lit.[34] 558K at 760mm Hg) then redistilled from itself; collecting the now water-white sulpholan. The purified sulpholan solidified to give a plastic-like material in the condenser which could be liquified at 299.5K; this behaviour has been reported previously[39].

Sulpholene (Aldrich Chemical Co. Ltd.) was supplied as pure white crystals. The melting point was determined and found to agree exactly with the literature value 338-339K.[34]

Acid chlorides used during the work were all purified by an efficient fractional distillation technique in which only the middle fractions were collected. Table 5.1. records the respective temperatures and pressures at which the middle fractions were collected.

TABLE 5.1

ACID CHLORIDES DISTILLATION TEMPERATURES AND PRESSURES

Acid Chloride	Temperature (K)	Pressure (mmHg)	Literature Values[35]	
Acetyl	325	760	325	760
Chloroacetyl	378	760	378-379	760
Methane sulphonyl	333	1.0	434	760
Oxalyl	335.5	760	336-337	763
Sulphuryl	342	760	341-343	760
Thionyl	352	760	352	760

The following miscellaneous reagents were obtained from B.D.H. Ltd. and used without further purification during the course of the work: hydrogen peroxide (100 vols), m-chloroperoxybenzoic acid, acetic anhydride, glacial acetic acid, triethylamine, sodium molybdate and sodium tungstate.

1,6-Dibromohexane (Aldrich Chemical Co. Ltd.) was vacuum distilled before use and the middle fraction was collected at 419K (0.1mm Hg), (Lit.[34] 516K at 760mm Hg).

Thietan (Trimethylene sulphide) (Aldrich Chemical Co. Ltd.) was distilled before use and the middle fraction was collected at 367K (760mm Hg), (Lit.[34] 367-367.5K at 760mm Hg).

1-Bromobutane (Aldrich Chemical Co. Ltd.) was distilled before use and the middle fraction was collected at 375K (760mm Hg), (Lit.[34] 373-377K at 760mm Hg).

5.2. Apparatus

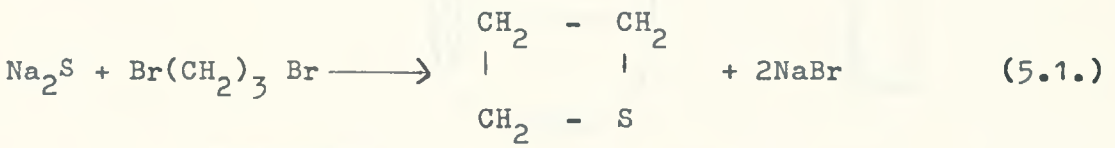
Throughout the sulphur work, as with the study on block co-polymer systems (Part A) reactions were carried out under nitrogen. High vacuum techniques were not employed. The apparatus used for the preparations of the sulphone "monomers", polymerisation testing, and copolymerisation investigations was similar to that used for experiments in Part A.

5.3. Preparation of the Four-Membered Cyclic Sulphones

A detailed discussion of the spectroscopic and physical properties of the sulphones prepared in this work is given in Chapter 6.

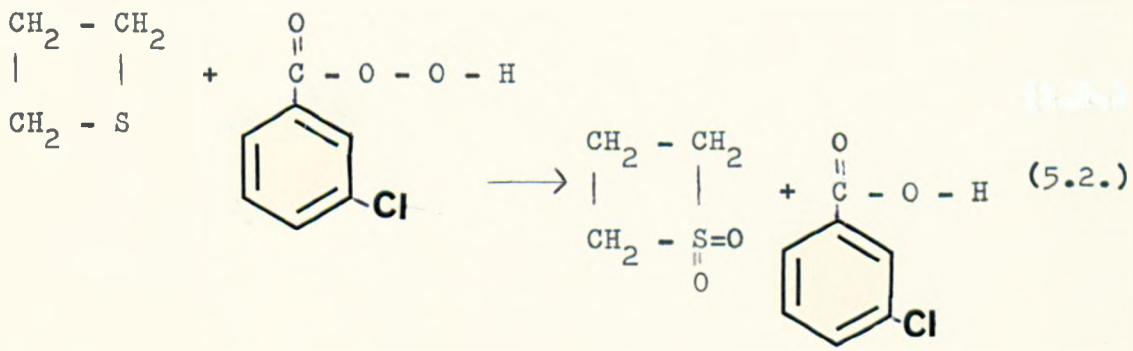
5.3.1. Thietan-1,1-dioxide

The general apparatus used for the preparations of the four-membered cyclic sulphones is shown in Figure 5.1. The bulk of trimethylene sulphide used in this preparation was purchased. However, while awaiting delivery a sample was prepared according to Tamres method[40] (equation (5.1.)).



$$Na_2S + Br(CH_2)_3Br \longrightarrow \begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ CH_2 - S \end{matrix} + 2NaBr \qquad (5.1.)$$

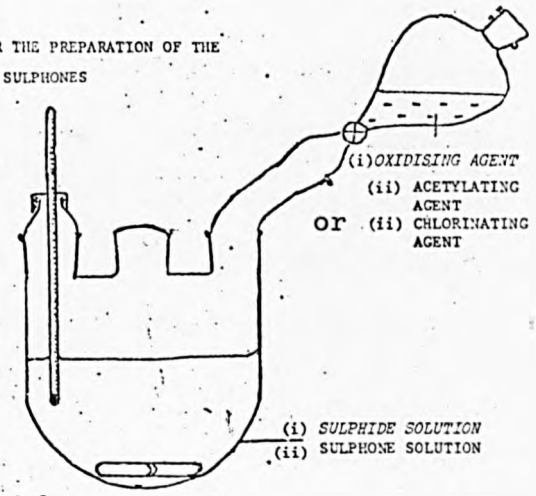
The trimethylene sulphide was oxidised to the sulphone by the method described below (equation (5.2.)).



$$\begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ CH_2 - S \end{matrix} + \begin{matrix} O \\ \| \\ C - O - O - H \end{matrix} \text{(Cl-C}_6\text{H}_4\text{)} \longrightarrow \begin{matrix} CH_2 - CH_2 \\ | \quad\quad | \\ CH_2 - S{=}O \\ \quad\quad\quad \| \\ \quad\quad\quad O \end{matrix} + \begin{matrix} O \\ \| \\ C - O - H \end{matrix} \text{(Cl-C}_6\text{H}_4\text{)} \qquad (5.2.)$$

FIGURE 5.1.

GENERAL APPARATUS FOR THE PREPARATION OF THE FOUR-MEMBERED CYCLIC SULPHONES



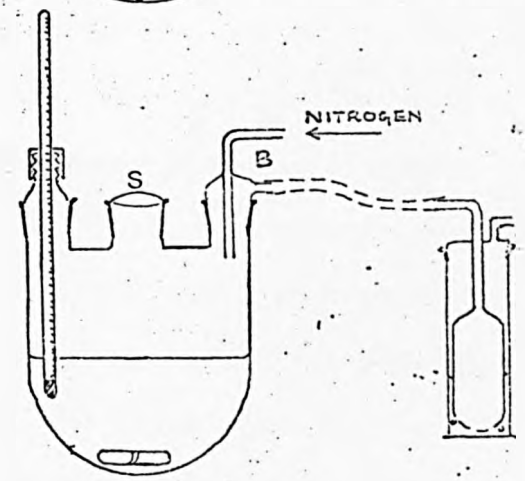
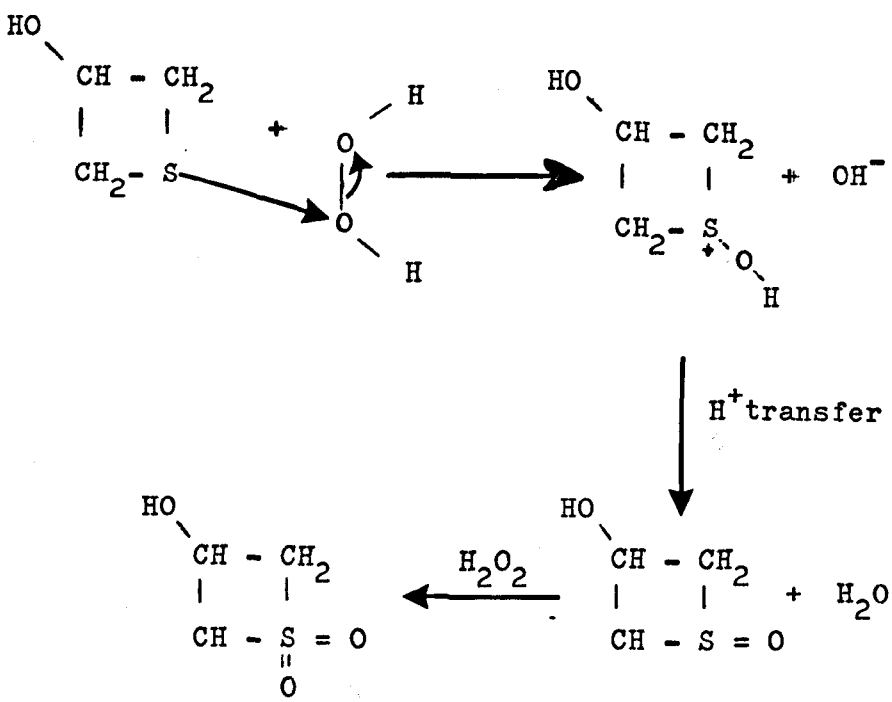


FIGURE 5.2.

APPARATUS FOR THE IONIC POLYMERISATION OF THE FOUR-MEMBERED CYCLIC SULPHONES.

(5.3.)


HO
CH - CH2
CH2- S
H
O
O
H
HO
CH - CH2
CH2- S
O
H
+ OH-
H+transfer
HO
CH - CH2
CH - S = O
+ H2O
H2O2
HO
CH - CH2
CH - S = O
O

m-Chloroperoxybenzoic acid (46.6g, 0.270 mole) in methylene chloride (100 ml) was added dropwise to a stirred solution of the trimethylene sulphide (10g, 0.135 mole) in methylene chloride (75ml) at 273K. The solution was stirred at this temperature for 12 hours and then filtered to remove the m-chlorobenzoic acid (equation (5.2.)). The filtrate was washed 3 times with 30ml of saturated sodium bi-carbonate solution, and dried over anhydrous sodium sulphate before evaporation of the methylene chloride to leave the sulphone (8.3g) as a white crystalline material. After recrystallisation from ethyl acetate, large white crystals were obtained, m.pt. 347.5K (Lit.[41] 346-348K yield 8.1g).

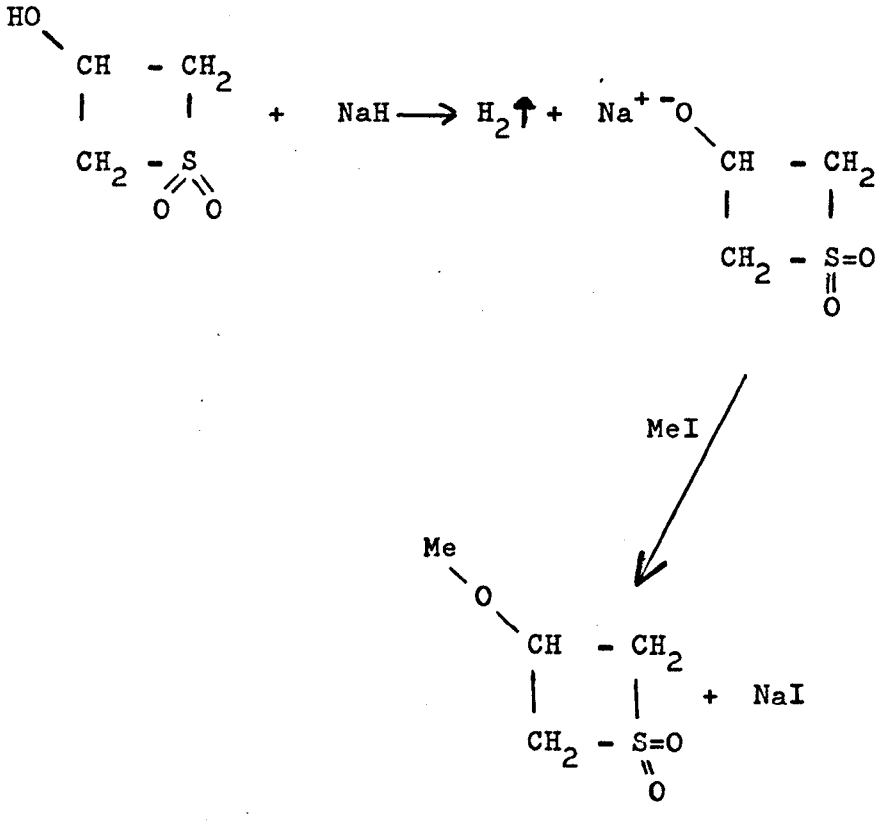
5.3.2. 3-Thietanol-1,1-dioxide

The preparation was based on a method reported by Lamm et al.[42] 3-Thietanol (30g, 0.33 mole) was dissolved in water (165 ml) containing sodium tungstate (0.66g) and glacial acetic acid (about 0.2ml); pH 4-5. The solution was stirred and the temperature held at 293K while hydrogen peroxide (80ml, approximately 0.8 mole) was added during 1 hour (equation (5.3.)). The reaction mixture was watched for 5 hours, with the temperature kept at 293K. It was then left for 12 hours at room temperature.

Alterations to the procedure reported above were carried out in separate experiments. For example, sodium tungstate was replaced by sodium molybdate, and the reaction time after the addition of peroxide was varied, but no increase in the 25g yield (61%) of 3-thietanol-1,1-dioxide resulted.

The isolation procedure involved destruction of excess peroxide with a catalytic amount of palladium on carbon; a sample of the solution was withdrawn and tested for peroxides[43]. After a

(5.4.)


HO
CH - CH2
CH2 - S
O O
+ NaH
H2
+ Na+ -O
CH - CH2
CH2 - S=O
O
MeI
Me
O
CH - CH2
CH2 - S=O
O
+ NaI

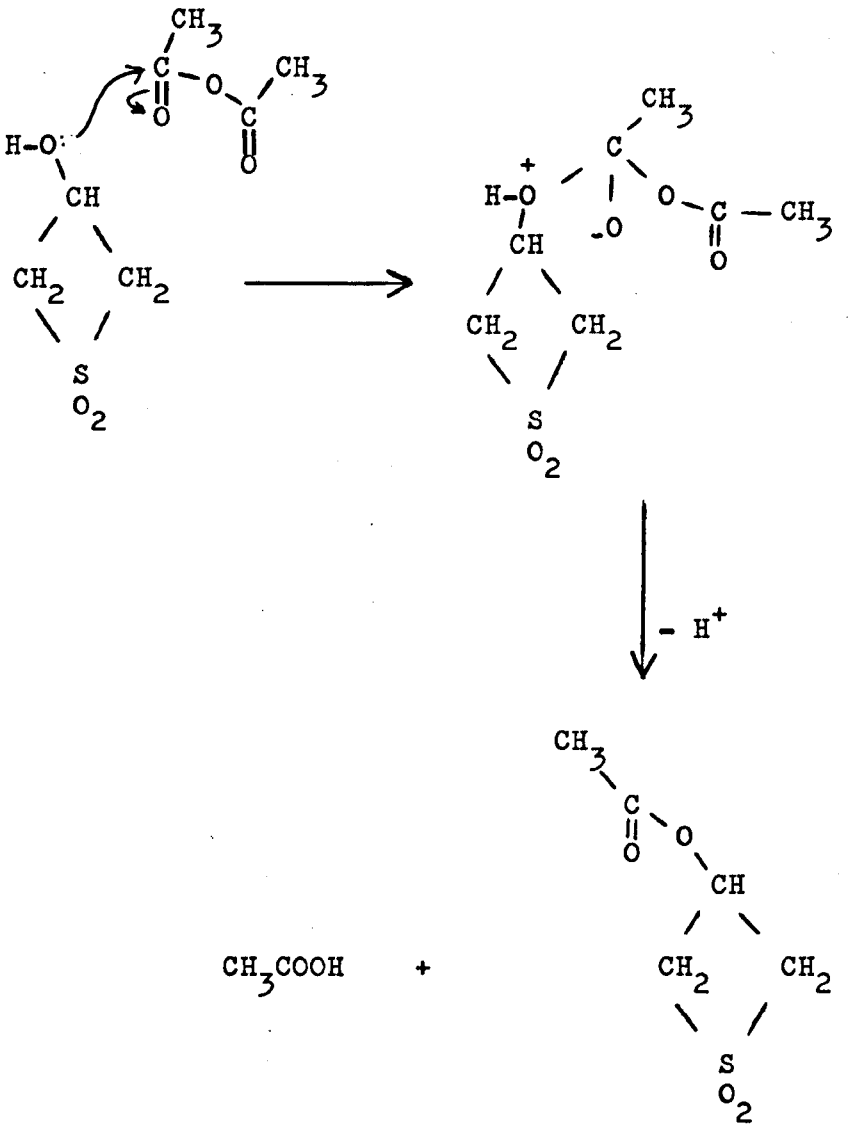
negative peroxide test, the colourless solution was evaporated in vacuo at a temperature below 323K. Since explosions have been reported in a similar preparation in which acetic acid and hydrogen peroxide were used, appropriate precautions were taken in case of such an occurrence[44].

The residue after evaporation consisted of a crystalline material and an oil. Recrystallisation of the crystalline material from ethyl acetate afforded white crystals m.pt. 373K (lit.[4] 372.5-375K, yield 25g).

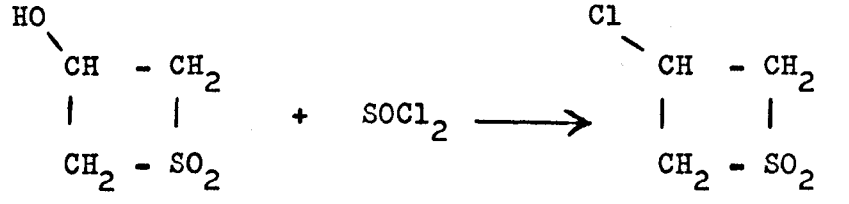
5.3.3. 3-Methoxythietan-1,1-dioxide

3-thietanol-1,1-dioxide (3g, 0.025 mole) was dissolved in THF (20ml), under nitrogen, at room temperature and 5ml of a THF solution of sodium hydride (0.60g, 0.025 mole) was added. After 5 minutes, methyl iodide (3.6ml, 0.025 mole) was added by syringe, and the mixture was kept at 303K for 1 hour (equation(5.4.)). Precipitation of a white solid was observed; this was found to be sodium iodide: simple qualitative tests[45] were performed to test for the presence of sodium and iodide ions; no organic material was detected in the precipitate.

Removal of the precipitate by filtration, and evaporation of the THF gave a white crystalline solid, which was recrystallised from ether plus hexane (2:1) to give large white crystals, m.pt. 333-335K, yield 2.45g.



(5.5.)



(5.6.)

5.3.4. 3-Acetoxythietan-1,1-dioxide

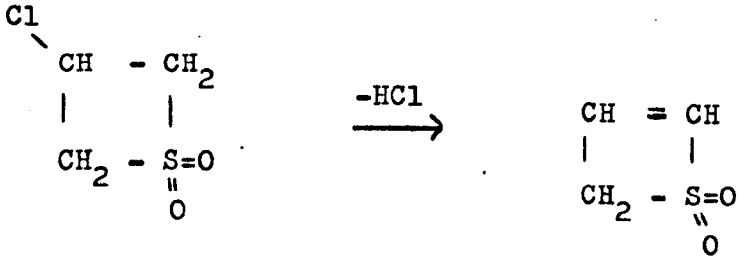
Acetic anhydride (3ml, 0.03 mole) was added to 3-thietanol-1,1-dioxide (3g, 0.025 mole) in acetic acid (25ml) and the mixture was refluxed for 2 hours (equation (5.5)). After which most acetic acid was removed by rotary evaporation to leave a white crystalline solid, that smelt of acetic acid. The solid was dissolved in ethyl acetate, then washed twice with a 5% sodium carbonate solution and washed finally with water. The organic layer was separated and dried over anhydrous sodium sulphate. The dried solution was filtered and evaporated to dryness to yield a crystalline solid which was recrystallised from absolute ethanol to give large white crystals m.pt. 394.5-396.5K, yield 2.3g.

5.3.5. 3-Chlorothietan-1,1-dioxide

The method used was a modification of the Dittmer et al. procedure[4]. Thionyl chloride (12g, ~0.1 mole) was added dropwise to a rapidly stirred suspension of 3-thietanol-1,1-dioxide (6.1g 0.05 mole) in dry s-collidine, the temperature being maintained at 273-278K. The reaction mixture was allowed to warm-up to room temperature when the addition had been completed (equation (5.6)). A viscous brown mixture was formed upon standing at room temperature for 0.5 hour but became fluid when heated on a steam bath for 0.75 hour. The hot solution was poured onto crushed ice, and a light brown solid product was formed which was washed with ice-water and crystallised from water after decolouration by charcoal to yield white, needle shaped crystals, m.pt. 409.5K and yield 5.7g (Lit.[4] m.pt. 409.5-410.5K and yield 6.1g).

Other chlorinating reagents were used (PCl_5 and PCl_3) in attempts to increase the yield, but were not successful.

(5.7.)



5.3.6. Preparation of 2-thiete-1,1-dioxide

Several preparative routes were investigated to obtain high yields of the unsaturated 2-thiete-1,1-dioxide. These included dehydration reactions which involved 3-thietanol-1,1-dioxide with (i) concentrated sulphuric acid and (ii) ortho-phosphoric acid. Other methods tested were (a) elimination of acetic acid from the 3-acetoxythietan-1,1-dioxide and (b) dehydrohalogenation of 3-chlorothietan-1,1-dioxide. For each system the yield of 2-thiete-1,1-dioxide was less than the 63% found for the Dittmer method[4] (equation (5.7)). A record of the yields obtained from the various systems is given in Table 5.2.

5.3.7. Thietan-1-oxide

The apparatus used for the preparation is shown in Figure 5.1. m-Chloroperoxybenzoic acid (23.3g, 0.135 mole) in methylene chloride (50ml) was added dropwise to 75ml of a stirred methylene chloride solution of trimethylene sulphide (10g, 0.135 mole) at 273K. The solution was left overnight and then filtered, before neutralisation of the filtrate with sodium bi-carbonate. The organic layer was separated and dried over anhydrous sodium sulphate. Evaporation of the methylene chloride left an oil which was vacuum distilled; the middle fraction had a boiling range 309-311K (760mm Hg) yield 7.4g, (Lit.[41] 309-311K at 760mm Hg and yield 8.0g).

TABLE 5.2

THE PERCENTAGE YIELDS FOR THE DIFFERENT METHODS USED TO PREPARE 2-THIETE-1,1-DIOXIDE.

	METHOD	% YIELD
(i)	Dehydration with concentrated sulphuric acid	<20
(ii)	Dehydration with ortho-phosphoric acid	<20
(iii)	Elimination of acetic acid from 3-acetoxythietan-1,1-dioxide	0
(iv)	Dehydrohalogenation of 3-chlorothietan-1,1-dioxide	60

5.4. Polymerisation Tests

5.4.1. General procedure for the attempted ionic polymerisation of the four-membered cyclic sulphones

The apparatus used for the ionic polymerisation tests is shown in Figure 5.2. All the cyclic sulphones were tested with butyl lithium and boron trifluoride etherate as the standard anionic and cationic initiators respectively. The radical polymerisation tests were undertaken with benzoyl peroxide as the catalyst. Other initiators used were; sodium naphthalene, lithium fluorenyl, titanium tetrachloride, stannic chloride, perchloric and trifluoroacetic acids; often solubility difficulties precluded their general employment. Table 5.3 records the various monomer/initiator permutations which were tried.

The use of "reaction blanks" was customary where appropriate. Reaction times were increased if the polymerisation tests proved negative, until periods of 36 hours became routine. A wide temperature range for the tests was covered by the careful selection of temperatures, i.e. 243K, 273K, 298K and 303K. Certain variations in reaction conditions were necessary if the temperature range was to be covered. For example, in the high temperature cationic polymerisation tests a solvent change was necessary; nitrobenzene was substituted for methylene chloride.

Polymerisation tests were repeated several times at one temperature with a different sample of solvent, or initiator, or sulphone for each experiment. A typical procedure for an ionic polymerisation test is described below.

The sulphone (0.02 mole) was dissolved in the solvent (50ml)- THF for the anionic and methylene chloride, or nitrobenzene for

TABLE 5.3

INITIATORS USED FOR THE ATTEMPTED POLYMERISATION OF THE FOUR-MEMBERED CYCLIC SULPHONES

Compound	5.3.1.	5.3.2.	5.3.3.	5.3.4.	5.3.5.	5.3.6.
Cationic Initiator	$BF_3OEt_2/HClO_4$ and CF_3COOH	$BF_3OEt_2/HClO_4$ and CF_3COOH	BF_3OEt_2/CF_3COOH	BF_3OEt_2	BF_3OEt_2	BF_3OEt_2/CF_3COOH $SnCl_4/TiCl_4$ and H_2SO_4
Anionic Initiator	$BuLi/Na^+/LiFl.$	BuLi	$BuLi/Na^+$	$BuLi/Na^+$		$BuLi/NaN/Na^+$
Free Radical Initiator	Bz_2O_2	Bz_2O_2	Bz_2O_2	Bz_2O_2	Bz_2O_2	Bz_2O_2

the cationic experiments. Solutions were brought to the reaction temperature and the initiator was added rapidly by syringe. The mixture was left for a stipulated period, during which time samples were removed with a syringe for p.m.r. analysis, to follow any polymerisation which might occur. At the end of the chosen period water was added, the organic layer was separated and dried with anhydrous calcium sulphate. The solvent was evaporated and the residue was analysed spectroscopically. In all experiments it was found to be the starting material.

When nitrobenzene was employed as the solvent, the reaction mixture was steam distilled to obtain the product.

A blank experiment was conducted simultaneously with the polymerisation tests and involved an identical reaction mixture but without initiator.

5.4.2. General procedure for the attempted free radical polymerisation of the four-membered cyclic sulphones

Attempts to polymerise the substituted thietan-1,1-dioxides and thiete-1,1-dioxide by radicals were carried out by benzoyl peroxide with and without u.v. light. Both types of experiment had reaction times measured in days rather than hours.

A general method for these experiments is given below. The cyclic sulphone (0.02 mole) was dissolved in benzene (50ml) under nitrogen and 5ml of a freshly prepared benzene solution of benzoyl peroxide (0.484g, 0.002 mole) was added by syringe. The mixture was heated at 333K under nitrogen.

Reactions which involved u.v. light were carried out in a similar manner but with the addition of a u.v. light source.

Experiments were also performed with u.v. light as the sole potential initiator. These were run at room temperature in stoppered quartz test tubes under a u.v. light source for periods up to 16 days.

Samples (5ml) were withdrawn at selected intervals and injected into methanol (20ml); evaporation of the solvents left a solid which was submitted for p.m.r. analysis.

5.4.3. Procedure for the attempted anionic polymerisation of sulpholan

The typical experimental procedure carried out for the attempted anionic polymerisation of sulpholan is given below. Sulpholan (2.4g, 0.02 mole) was dissolved in THF (50ml), under nitrogen, and cooled to 273K, a solution of butyl lithium in THF (0.5ml, 0.0 01 mole) was then added by syringe.

This procedure was repeated with separate samples at 243K and 323K, the isolation technique used was described in section 5.4.1.

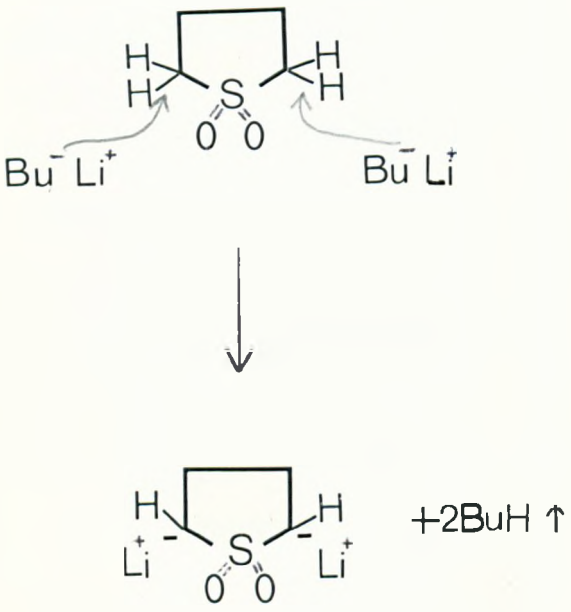
P.m.r. and C, H elemental analyses were consistent with unreacted sulpholan being the only product obtained in all experiments. (see section 6.3.).

5.4.4. Procedures for the anionic polymerisation of thietan-1-oxide

A single anionic polymerisation test was carried out on thietan-1-oxide by a similar method as described in section 5.4.1. but the experiment was performed in a p.m.r. tube and at 293K.

There was no evolution of heat, and no change in the p.m.r. spectrum of the starting material after one hour.

(5.8.)



5.5. Copolymerisation Studies

5.5.1. Preparation of the sulpholan α,α'-dianion

The method used was a modification of the Truce and Klingler procedure[30].

A reaction was carried out to generate the sulpholan dianion (equation (5.8.)). The apparatus used is shown in Figure 2.1. sulpholan (6g 0.05 mole) was dissolved in THF (250ml), under nitrogen, and cooled to 283K. Butyl lithium (50ml, 0.1 mole) in hexane was added slowly to the solution. After about two-thirds of the butyl lithium had been added some precipitation was observed. No precipitation occurred when butyl lithium in THF was used. Although this latter reagent was difficult to prepare it was used in preference to butyl lithium in hexane, and was employed in experiments for which higher yields of pure compounds were required. The experiment was followed conductimetrically and the onset of precipitation corresponded to the maximum conductance recorded. Samples (25ml) were withdrawn periodically by syringe, injected into deuterium oxide and submitted for p.m.r. analysis. The concentration and behaviour of the dianion as a function of time was thereby determined.

5.5.2. Procedure for the preparation of low molecular weight sulpholan di-adducts

The sulpholan α,α'-dianion was prepared as described in section 5.5.1. (equation(5.8.)) in the apparatus in Figure 2.3. Methane sulphonyl chloride (23.5ml, 0.3 mole) in THF (100ml) was kept under nitrogen in flask G at 283K. The sulpholan dianion solution was transferred from flask H to G by nitrogen pressure. (the reason for this method of addition is given later in Section 6.3.) The acetyl chloride derivative was also prepared in this way. The desired products were obtained by a series of water-methylene chloride extractions, the organic layer was dried over anhydrous sodium sulphate and the solvent removed. The oily

residue was separated by preparative thin and column chromatography to yield unreacted sulpholan and a fraction which contained the required product. Preparative g.l.c. was then used to obtain a sample of the pure low molecular weight adduct for p.m.r. analysis.

5.5.3. Procedure for the copolymerisation of sulpholan and a series of linking agents

The sulpholan dianion was prepared as reported in section 5.5.1. (equation (5.8.)) and the linking agent (0.05 mole) was introduced by syringe into the solution.

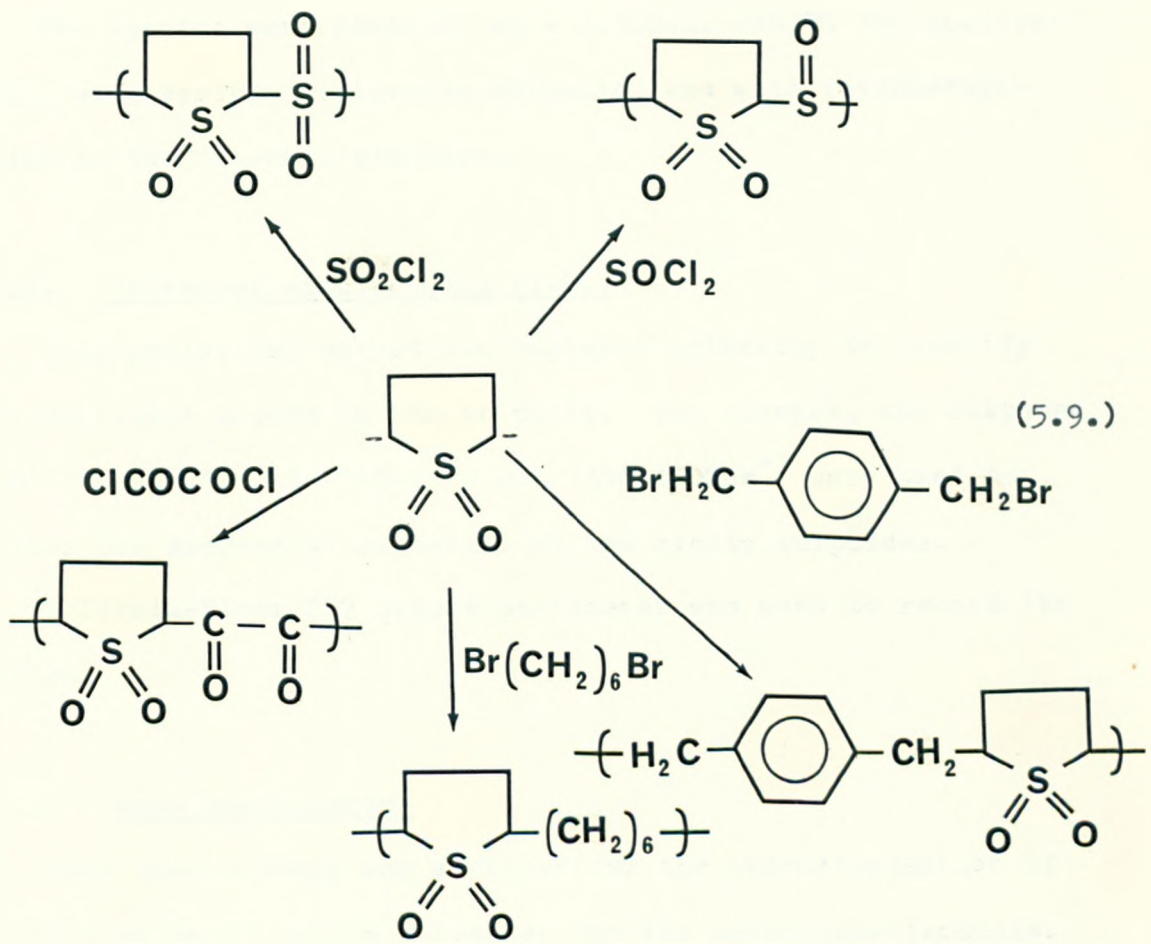
The linking agents used were difunctional species capable of reacting with the sulpholan dianion to produce an alternating copolymer; they included dibromohexane, sulphuryl chloride, thionyl-chloride,oxalyl chloride and p-xylylene dibromide (equation (5.9.)).

The copolymerisations were conducted at 223K, 253K and 273K, in an effort to observe any temperature dependence.

A reaction is described in which thionyl chloride was the linking agent used; the observations recorded were common to all the copolymerisation reactions.

When the thionyl chloride (3.65ml, 0.05 mole) was added rapidly to the stirred sulpholan dianion solution, an immediate colour change from yellow to dark brown was seen, and precipitation occurred simultaneously. The conductivity decreased very quickly to what it had been before the addition of butyl lithium was made.

The copolymeric products were isolated in methanol, filtered and dried in a vacuum oven at 323K before analysis. The results of the various analyses performed on each copolymer are given in section 6.4.



(5.9.)

5.6. Analytical Techniques

5.6.1. Proton and carbon 13 magnetic resonance spectroscopy

These techniques were used to verify the structure of the four-membered cyclic sulphones, the copolymeric products, the small molecular weight sulpholan diadducts and to record the fate of the dianion, once produced, as a function of time.

The spectra were recorded on a J.E.O.L. JNM,FX 100 spectrometer, with various deuterated solvents, and with tetramethylsilane as the internal standard.

5.6.2. Infra-red spectroscopy (I.R.)

This analytical method was employed primarily to identify the functional groups in the products. For example, the sulphone (S=O) frequencies at 1160-1140 and 1350-1300cm^{-1} were used to monitor the successful oxidation of the cyclic sulphides.

A Perkin-Elmer 257 spectrophotometer was used to record the spectra.

5.6.3. Mass spectroscopy

Mass spectroscopy was employed for the characterisation of the four-membered cyclic sulphones and the sulpholan-diadducts. Only the fragmentation patterns were recorded, on the Hitachi Perkin Elmer RMU6 Mass Spectrometer.

5.6.4. Carbon and hydrogen elemental analysis

This technique was used after the subject compound had been obtained in a pure state.

The instrument used for the analysis was a Perkin-Elmer 240 Elemental Analyzer.

5.6.5. Melting points (m.pt.)

All melting points were determined on a Reichert Microscope Melting Point apparatus, the recorded values being used as a measure of the compound's purity.

5.6.6. Differential scanning calorimetry (D.S.C.)

Analysis was carried out on the copolymers:

The temperature at which decomposition occurred was recorded on a Perkin-Elmer DSC-1 instrument.

5.6.7. Gas-liquid chromatography (g.l.c.)

The purity of reagents before reaction was checked, and the number of components in a mixture ascertained by use of this technique. A Hewlett Packard 5700A Gas Chromatograph fitted with a column packed with 1% OV 101 on 80/100 mesh "Chromosorb G" was used.

5.6.8. Thin layer chromatography

This analytical method provided a complementary means of determining the number of components in a mixture. A silica support (Kieselgel 60PF 254) with a polymeric binder was used to prepare the preparative and thin layer plates.

5.6.9. Preparative - thin layer and column chromatography

Both of these techniques were employed in purification of the copolymers and low molecular sulpholan diadducts. A maximum of 250mg of material could be loaded onto the preparative thin layer plates (40cm x 20cm), while the limit for the columns was 10g per 100g of alumina (activity 4).

5.7. Testing for Biological Activity

All the sulphone compounds prepared in this study were submitted to the I.C.I. Plant Protection Division for testing for various kinds of biological activity.

References to CHAPTER 5.

34. "Aldrich Catalogue Handbook of Organic and Biochemicals", 1977-1978.

35. D.D. Perrin, W.L.F. Armarego and D.R. Perrin, "Purification of Laboratory Chemicals" Pergamon Press, LONDON, 1966.

36. H. Gilman and A.H. Haubein, J. Amer. Chem. Soc., 1944, 66, 1515.

37. M. Morton and L.J. Fetters, "Anionic Polymerisation of Vinyl Monomers", Rubber Chemistry and Technology, 1975, 48, (3), 359.

38. Robinson Brothers Ltd., Data Sheet on 3-thietanol.

39. L. Jannelli, M. Della Monica and A. Della Monica, Gazz. chim. ital., 1964, 94, (5), 552.

40. M. Tamres and S. Searles, J. Amer. Chem. Soc., 1959, 81, 2100.

41. Y. Etienne, R. Soulas and H. Lumbroso, "Thietane and its Derivatives", Heterocyclic Compounds, 2, Interscience, 1964.

42. B. Lamm and K. Gustafsson, Acta Chem. Scand. (B), 1974, 28, (b), 701.

43. H.L. Jackson, W.B. McCormack, C.S. Rondestvedt, K.C. Smeltz and I.E. Viele, J. Chem. Ed., 1970, 47, (3), A180.

44. D.C. Dittmer, M.E. Christy, N. Takashina, R.S. Henion and J.M. Balquist, J. Org. Chem., 1971, 36, (9), 1324.

CHAPTER 6

RESULTS AND DISCUSSION

6.1. Characterisation of the Four-Membered Cyclic Sulphones

The sulphones synthesized in the present study are: Thietan-1, 1-dioxide, 3-thietanol-1,1-dioxide, 3-methoxythietan-1,1-dioxide, 3-acetoxythietan-1,1-dioxide, 3-chlorothietan-1,1-dioxide and thiete-1,1-dioxide, and all of them are known i.e. they have either been prepared for spectroscopic studies[45] or as intermediates in a multi-stage synthesis[4].

The spectroscopic and physical data published on these sulphones (Table 6.1.) are listed in reviews on thietan-1,1-dioxides[47], or in investigations of selected members which exemplify the trends observed with a particular type of substituent[45,48]. Each of the sulphones prepared in this work was characterised and the results are compared with published data.

6.1.1. P.m.r. spectra of the four-membered cyclic sulphones

The p.m.r. spectra of the different sulphones which are listed in section 6.1. agreed closely with the published data[45,46,48]. From the p.m.r. study the following conclusions are drawn: Firstly, the sulphones were of high purity (>95%) as evinced by the absence of peaks due to "impurities". (The word "impurities" as used in this chapter is meant to denote unwanted products, as well as material which is present from the beginning of a synthesis.) Secondly, the chemical shifts of the methylene protons in the thietan-1,1-dioxides and the olefinic protons in thiete-1,1-dioxide (Figure 6.1.) are different and give rise to a more complicated splitting pattern than was predicted from first examination.

A general trend can be observed in the data in Table 6.2.

FIGURE 6.1.

RING CONFIGURATION OF THE FOUR-MEMBERED SULPHONES

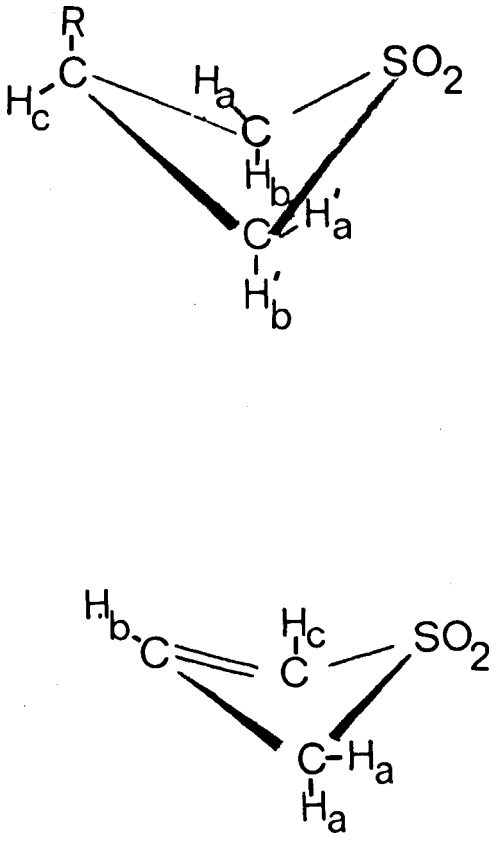


TABLE 6.1

CHARACTERIZATION OF FOUR-MEMBERED CYCLIC SULPHONES.

	Compound/Analysis	M.p./K Recorded	Lit.	C,H (%) Theoretical	C,H (%) Actual	I.R.	P.M.R.	M.S.
A	Thietan-1,1-dioxide	347.5	346-348[41]	C=33.96 H= 5.66	C=34.06 H= 5.80	Ref. 47	Ref. 46	Fig. 6.3
B	3-Thietanol-1,1-dioxide	373	372.5-375[4]	C=29.5 H= 4.9	C=29.72 H= 4.96	Ref. 47	Ref. 45	Fig. 6.3
C	3-Methoxythietan-1,1-dioxide	383-385	-	C=26.47 H= 5.88	C=27.15 H= 6.02	Ref. 47	Ref. 46	-
D	3-Acetoxythietan-1,1-dioxide	394.5-396.5	-	C=36.70 H= 5.06	C=36.59 H= 4.88	Ref. 47	Ref. 45	-
E	3-Chlorothietan-1,1-dioxide	409.5	409.5-410.5[4]	C=25.6 H= 3.56	C=25.53 H= 3.60	Ref. 47	Ref. 45	-
F	2-Thiete-1,1-dioxide	326	325-327[4]	C=34.6 H= 3.85	C=35.5 H= 3.99	Ref. 47	Ref. 4	

TABLE 6.2

CHEMICAL SHIFTS(δ) OF THE PROTON ABSORPTIONS IN THE P.M.R. SPECTRA OF FOUR-MEMBERED CYCLIC SULPHONES.

	H_A	H_B	H_C	OH-	CH_3CO_2-	CH_3O-
Thietan-1,1-dioxide	3.5	3.8	3.8	-	-	-
3-Thietanol-1,1-dioxide	3.9	4.4	4.6	5.9	-	-
3-Methoxythietan-1,1-dioxide	3.9	4.3	4.8	-	-	3.4
3-Acetoxythietan-1,1-dioxide	4.2	4.6	5.3	-	2.1	-
3-Chlorothietan-1,1-dioxide	4.4	4.9	4.9	-	-	-
2-Thiete-1,1-dioxide	4.58	7.38	7.04	-	-	-

Thietan-1,1-dioxide has its absorptions at the expected positions. The introduction of substituents into the C-3 position produces the predicted shift in the low field H_c absorption.

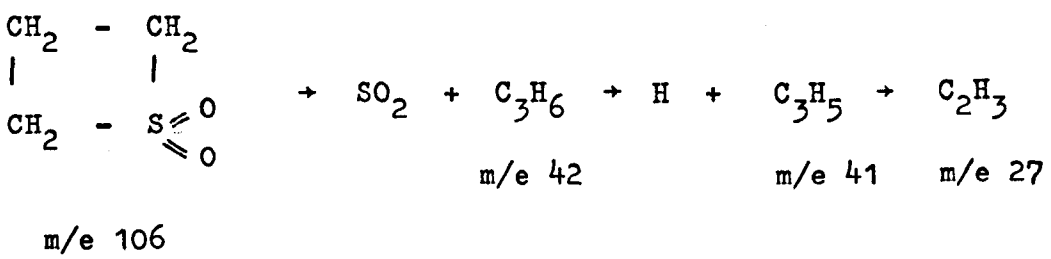
The O-H absorption at 5.9 δ was broad which means that there is inter rather than intra molecular hydrogen bonding.

6.1.2. Infra-red

Infra-red spectroscopy was used to confirm the presence of the characteristic absorptions of the subject sulphone by comparison with published data[47]. Figure 6.2. shows the spectrum obtained for the 3-chlorothietan-1,1-dioxide, which is typical of the spectra obtained for substituted thietan-1,1-dioxides.

6.1.3. Mass spectroscopy

This technique was used primarily to obtain a precise value of the molecular weight of each sulphone. However, the fragmentation pattern of thietan-1,1-dioxide (1) and 3-thietanol-1,1-dioxide (2) was observed: elimination of sulphur dioxide is always the initial step with charge retention on the resulting hydrocarbon fragment. The break-down pattern for (1) is given in Scheme A.



Molecular ion

Scheme A

FIGURE 6.2. I.R. spectrum of
3-chlorothietan-1,1-dioxide

FIGURE 6.2.

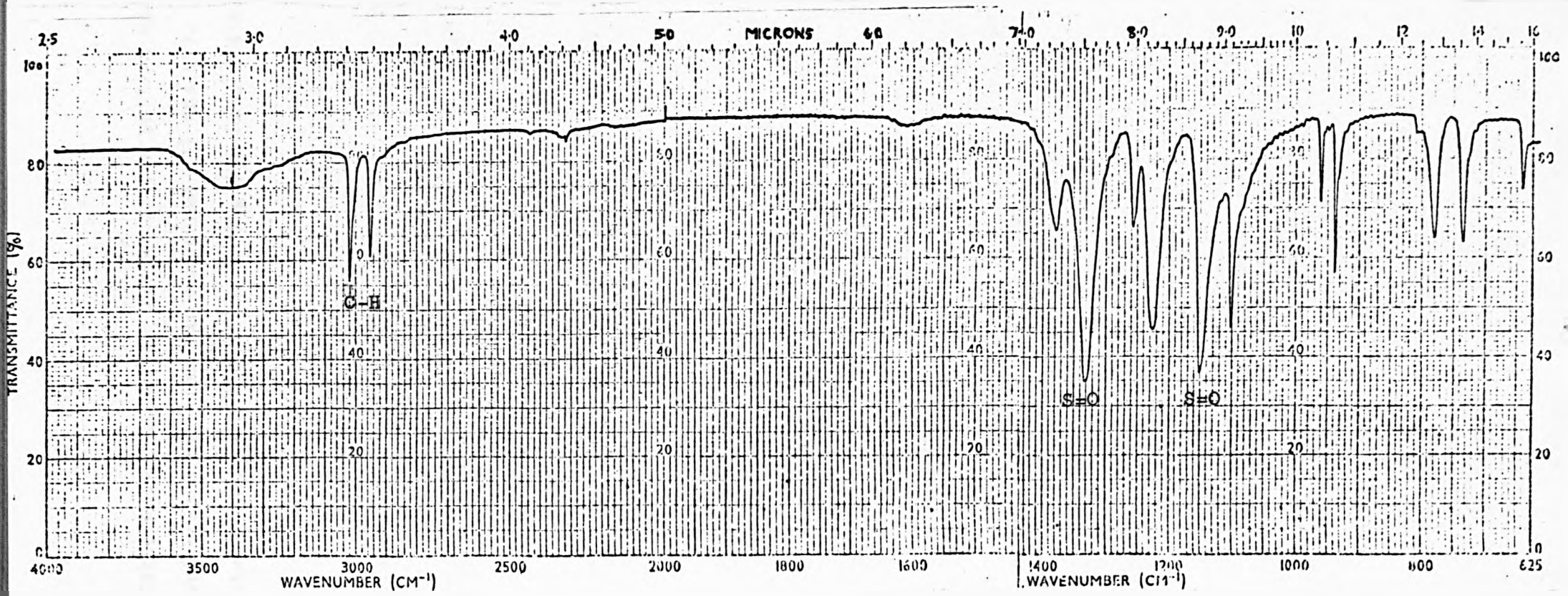

2·5
3·0
4·0
5·0
MICRONS
6·0
7·0
8·0
9·0
10
12
14
16
100
80
60
40
20
0
TRANSMITTANCE (%)
C-H
S=O
S=O
4000
3500
3000
2500
2000
1800
1600
1400
1200
1000
800
625
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)

Table 6.3. records the fragmentation pattern and the peak positions which were recorded for compounds (1) and (2). Computer traces of these results are plotted in Figures 6.3. and 6.4.

TABLE 6.3

PARTIAL* MASS SPECTRA OF SELECTED COMPOUNDS.

COMPOUND	m/e (INTENSITY)
Thietan-1,1-dioxide	27(17),28(50),41(100),42(82),106(35).
3-Thietanol-1,1-dioxide	27(12),29(15),44(100),57(12),58(10),122(17).

* Only peaks with intensities > 10% of the base peak are listed.

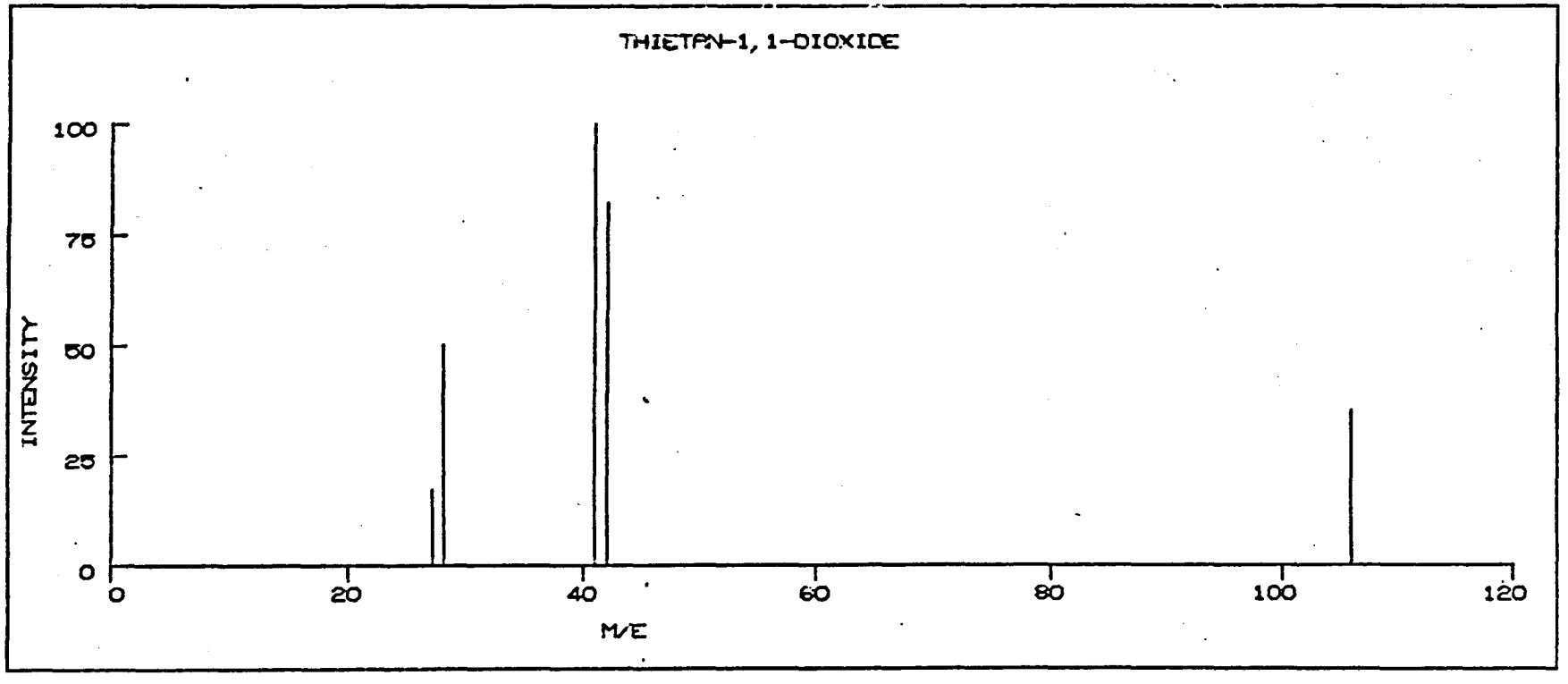

THIETAN-1, 1-DIOXIDE
INTENSITY
100
75
50
25
0
0
20
40
60
80
100
120
M/E

FIGURE 6.3.

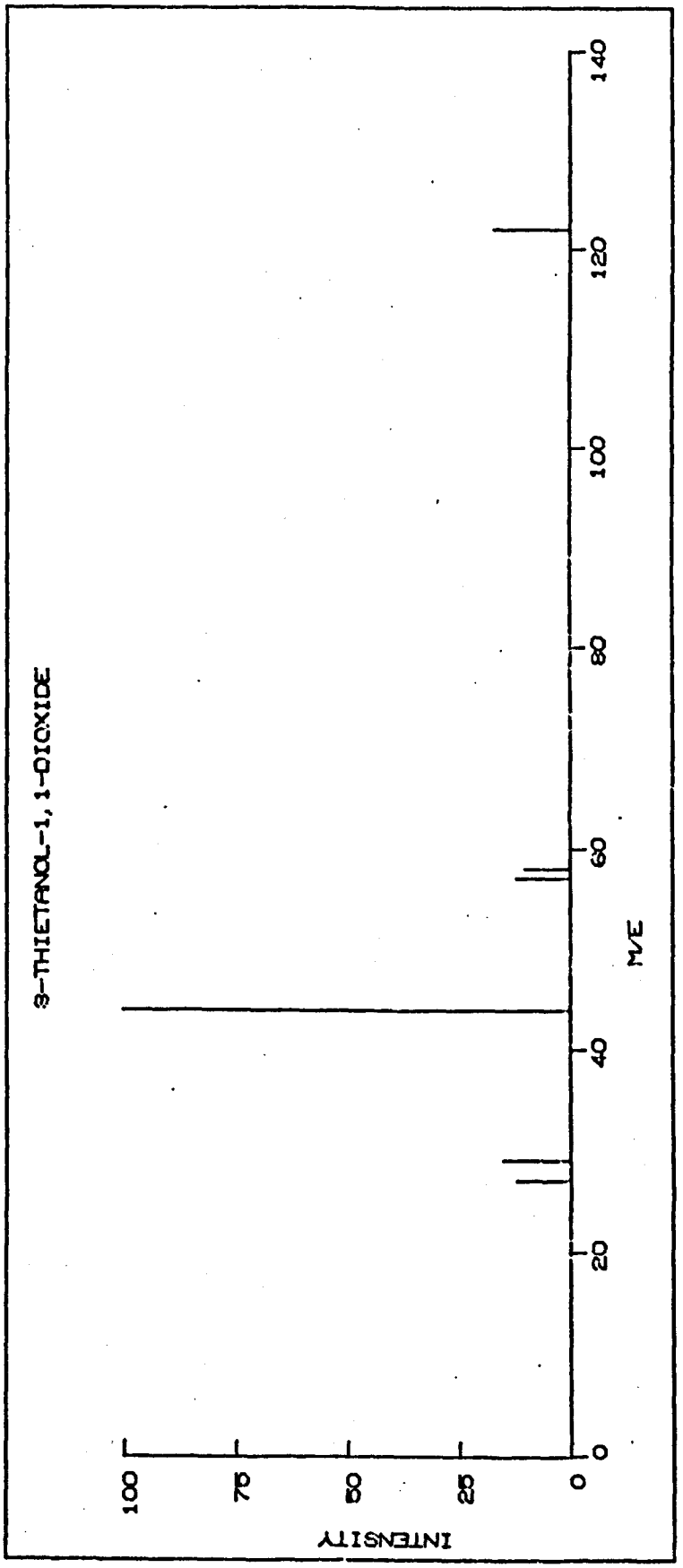

3-THIETANOL-1,1-DIOXIDE
INTENSITY
100
75
50
25
0
M/E
0
20
40
60
80
100
120
140

FIGURE 6.4.

6.2. Polymerisation Tests

Table 5.3. summarizes the initiators which were employed in attempts to polymerise the sulphones after they had been characterized.

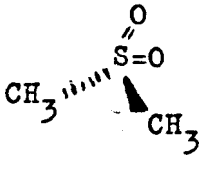
No polymerisation was observed for any of the four-membered sulphones.

These findings are disappointing but can be reconciled by comparison with other aliphatic sulphones which do not polymerise[12].

6.2.1. Discussion of results

To account for the unreactivity of the sulphones it is necessary to consider bonding between sulphur and the other atoms. One of the most important reasons why organosulphur compounds have properties which differ widely from those of analogous oxygen compounds that sulphur is substantially less electron attracting than oxygen. Further sulphur, unlike oxygen, is reluctant to form double bonds due to the weakness of $p\pi$-$p\pi$ overlap involving the 3p orbitals. However, the possibility of π-d bonding arises in the S=O bond; here in addition to a σ bond between the sulphur and oxygen a π bond is formed in which the oxygen lone pair utilizes the vacant sulphur d orbitals.

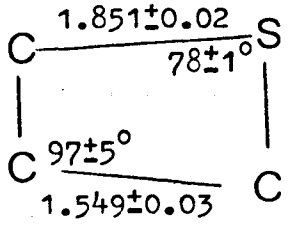
An important difference between ordinary $p\pi$ -$p\pi$ overlap and S=O double bonds with $p\pi$ -$d\pi$ overlap is the absence of any requirement in the latter case for the groups attached to sulphur to be coplanar. Thus dimethyl sulphone can adopt a non-planar configuration:



This argument can be applied to the four-membered cyclic sulphones. The thietan ring (Figure 6.5.) is virtually planar and possesses considerable ring strain[41]. Polymerisation of the thietans is therefore promoted by the ring strain and the ease of attack by various initiators on the planar system. The formation of the S=O bonds by expansion of the sulphur's valence shell allows the ring to adopt a more puckered configuration (Figure 6.1.). An x-ray analysis[49] found that the angle of puckering in the 3-acetoxy-thietan-1,1-dioxide was 18°. Therefore, the non-polymerisation of the cyclic sulphones in contrast to the thietans can be attributed to (1) the absence of ring strain and (2) the sulphur atom being in its higher oxidation state. Both of these changes have removed the driving force for a ring opening polymerisation process.

FIGURE 6.5.

SPATIAL CONFIGURATION OF THE THIETAN MOLECULE



Literature Data

C-S = 1.81± 0.01 Å[50]

C-S-C = 105° in dimethyl sulphide[41]

C-C = 1.54± 0.003 Å[50]

C-C-C = 109°28' in alkanes[41]

6.3. Sulpholan Dianion

The fate of the sulpholan dianion over a one hour period (section 5.5.1.) was followed by ^{13}C n.m.r. to determine whether any ring opening had occurred, since peaks were found in the p.m.r. spectra of the worked-up copolymers which corresponded to a sequence of linear methylene groups. However, it was later discovered by a member of staff of this Department (while working on phosphorus compounds) that these methylene units originated from a polymeric binding material in the silica, which was used for the T.L.C. and P.T.L.C. plates.

The C^{13} investigation revealed that within the time scale of the copolymer preparations no side reactions were occurring which involved ring opening. But after one hour peaks due to "impurities" were observed in the spectrum (Figure 6.6.).

The spectrum of a purified sample of sulpholan as shown in Figure 6.6.1.

6.3.1. Copolymeric products

Table 6.4. lists the results that were obtained from the analyses performed on the copolymeric products.

As shown in Figures 6.7. to 6.11. the peaks which were expected from the structure of the copolymers are present in the spectra, but peaks whose origins are unknown, are also evident. The C and H content of the copolymers is higher than expected; attempts to separate the "impurities" by column chromatography failed. This would suggest that the "impurities" may be attached to the polymer chain.

The conversion of monomer to polymer is low, but this can be accounted for by the precipitation of unreacted sulpholan with

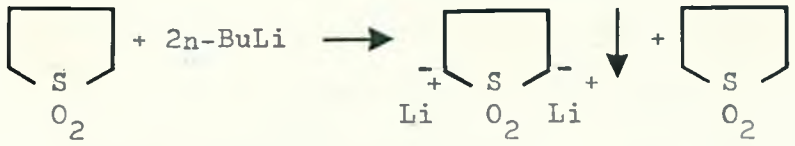
TABLE 6.4

CHARACTERIZATION OF THE SULPHOLAN COPOLYMERS

Dihalide	P.M.R.	I.R.	C,H (%) Theoretical	C,H (%) Actual	Softening Range/K	Molecular Weight	% Conversion (based on sulpholan)	Decomposition Temperature/K (Found by D.S.C.)
$Br-(CH_2)_6-Br$	Fig. 6.7	Fig. 6.9	C=59.4 H= 8.9	C=60.5 H= 9.3	412-418	30,000*	42	420
$SOCl_2$	Fig. 6.8	Fig. 6.9	C=29 H= 3.6	C=31.2 H= 3.67	278-283	20,000	45	390
SO_2Cl_2	Fig. 6.8	Fig. 6.9	C=26 H= 3.3	C=29.1 H= 3.74	283-288	20,000	45	-
Cl-C(=O)-C(=O)-Cl	Fig. 6.10	Fig. 6.9	C=37.5 H= 3.4	C=39.2 H= 3.85	303	587.5	18	-
Br-CH_2-C$_6$H$_4$-CH_2-Br	Fig. 6.11	Fig. 6.9	C=64.9 H= 6.3	C=66.6 H= 7.1	280-285	1262	20	-

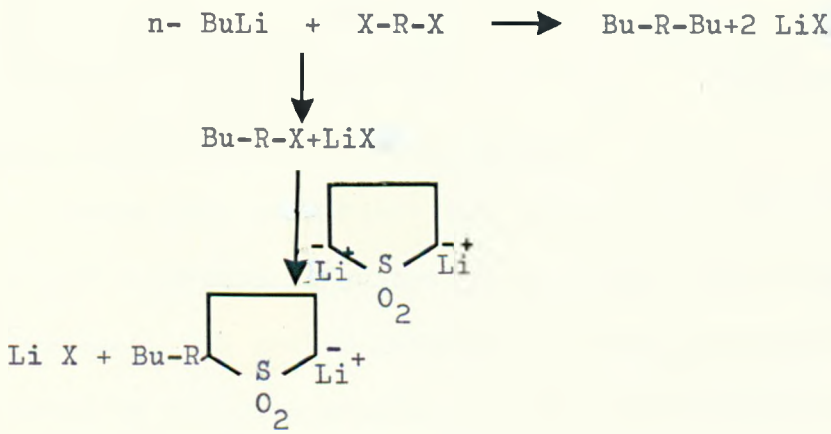
* Polystyrene equivalent found by g.p.c.

copolymer (see section 6.4.). When butyl lithium is added to the THF solution of sulpholan the dianion is generated, as evinced by the rapid rise in the conductivity and, after addition of approximately 70% of the stoichiometrically required volume of butyl lithium, precipitation of some dilithio-sulpholan salt occurs (equation (6.1.)).

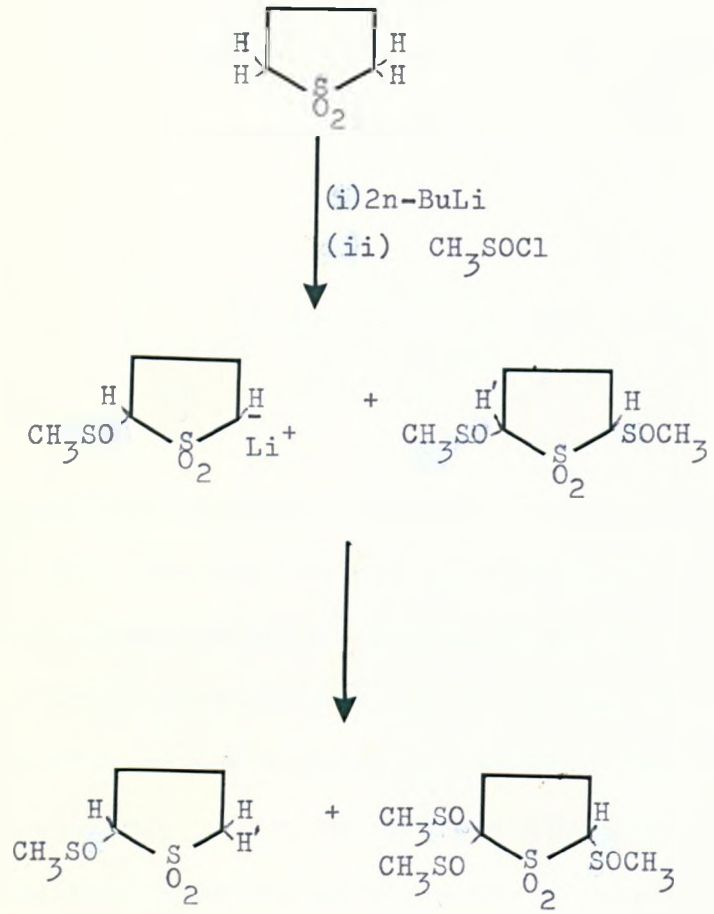


(6.1.)

Although approximately 30% of unreacted sulpholan remains in the reaction mixture, it could well be co-precipitated with dianion formed and therefore remain unexposed to the unreacted butyl lithium. Thus on addition of a dihalide, reaction would occur directly with the butyl lithium and involve one or both of the halide atoms. Reaction with both halide atoms yields a dibutyl adduct and with only one - the other halide atom reacting in the desired manner - a monohalide which acts as a chain stopper (equation (6.2.)).



(6.2.)



(6.3.)

Efforts to overcome the precipitation problem were moderately successful; halving the concentration reduced the precipitation by about 70-80% and increased slightly the DP. The use of solubilizing agents (N,N,N',N' - Tetramethyl-1,6-hexanediamine) specific for lithium gave no increase in the purity or in the yield of the copolymers.

The decomposition temperatures of two of the copolymers were recorded by D.S.C. and were found to be much lower than those reported for aromatic polysulphones[51]. The decomposition temperature of the copolymer which contained the pxylylene moiety was not recorded because (i) it was of lower M.W. and (ii) it was more impure compared with those copolymers analysed (Table 6.4.).

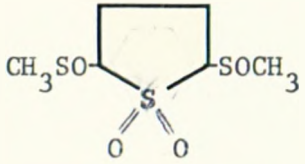
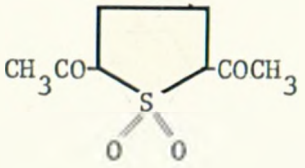
6.3.2. Low molecular weight sulpholan diadducts

Once it was clear that the copolymers were unlikely to be of commercial importance, attention was directed towards the biological aspects of low molecular sulpholan compounds. Before embarking on this investigation it was recognized that any impurities present in the products had to be removed, since only pure compounds are of use in biological systems. Therefore, a "reverse addition technique" was utilized (section 5.5.2.) to reduce the possibility of anion exchange reactions (equation (6.3.)). These reactions are probably responsible for some of the "impurities" obtained in the copolymers prepared by the previous technique.

Table 6.5. summarizes the results of analyses carried out on the new compounds 2,5-diacetylsulpholan and 2,5-dimethanesulphonyl sulpholan. The yields obtained are not quantitative as they are limited by the precipitation of unreacted sulpholan when butyl lithium in hexane is used. Precipitation is due to the low solubility of

TABLE 6.5

LOW MOLECULAR SULPHOLAN DIADDUCTS.

Compound	C^{13} N.M.R.	I.R.	C,H (%) Theoretical	C,H (%) Actual	M.p./K(deg.C)	Yield (%)
	Figure 6.14	Figure 6.13	C=21.75 H= 3.6	C=21.99 H= 3.78	390(167)	25
	Figure 6.12	Figure 6.13	C=47.0 H= 5.88	C=47.4 H= 6.04	392(169)	25

sulpholan in the THF/hexane system which results from (i) the increasing volume of hexane on adding the butyl lithium and (ii) the low temperature at which the reaction is carried out.

The C,H elemental analysis indicates that these products are very pure (>95%).

The ^{13}C n.m.r. spectra of the diadducts (Figures 6.12. and 6.14.) show the expected peaks. To obtain an accurate measurement for the intensity of the carbonyl absorption a relaxation reagent (chromium (III) acetylacetonate) was prepared[52] and added to the deuterated acetone solution of 2,5-diacetylsulpholan. The relaxation reagent allows carbon atoms which have no hydrogens attached to dissipate absorbed energy through the chromium atom, and so a realistic measure of the intensity of peaks due to the carbonyl group can be gained directly from the spectrum.

Figure 6.6. shows the ^{13}C n.m.r. completely decoupled spectrum (run in D_6 Acetone) of the water killed product from reaction of sulpholan with butyl lithium at 223K after one hour. Impurity peaks (I) can be observed in the spectrum.

FIGURE 6.6.

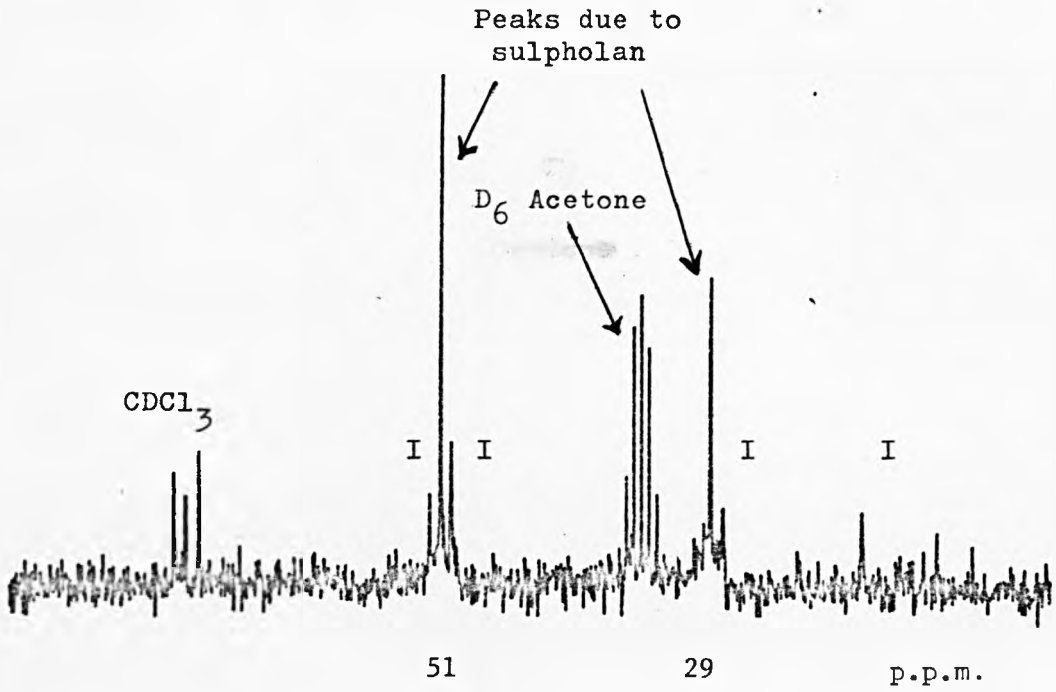


Figure 6.6.1. shows the p.m.r. spectrum of sulpholan

FIGURE 6.6.1.

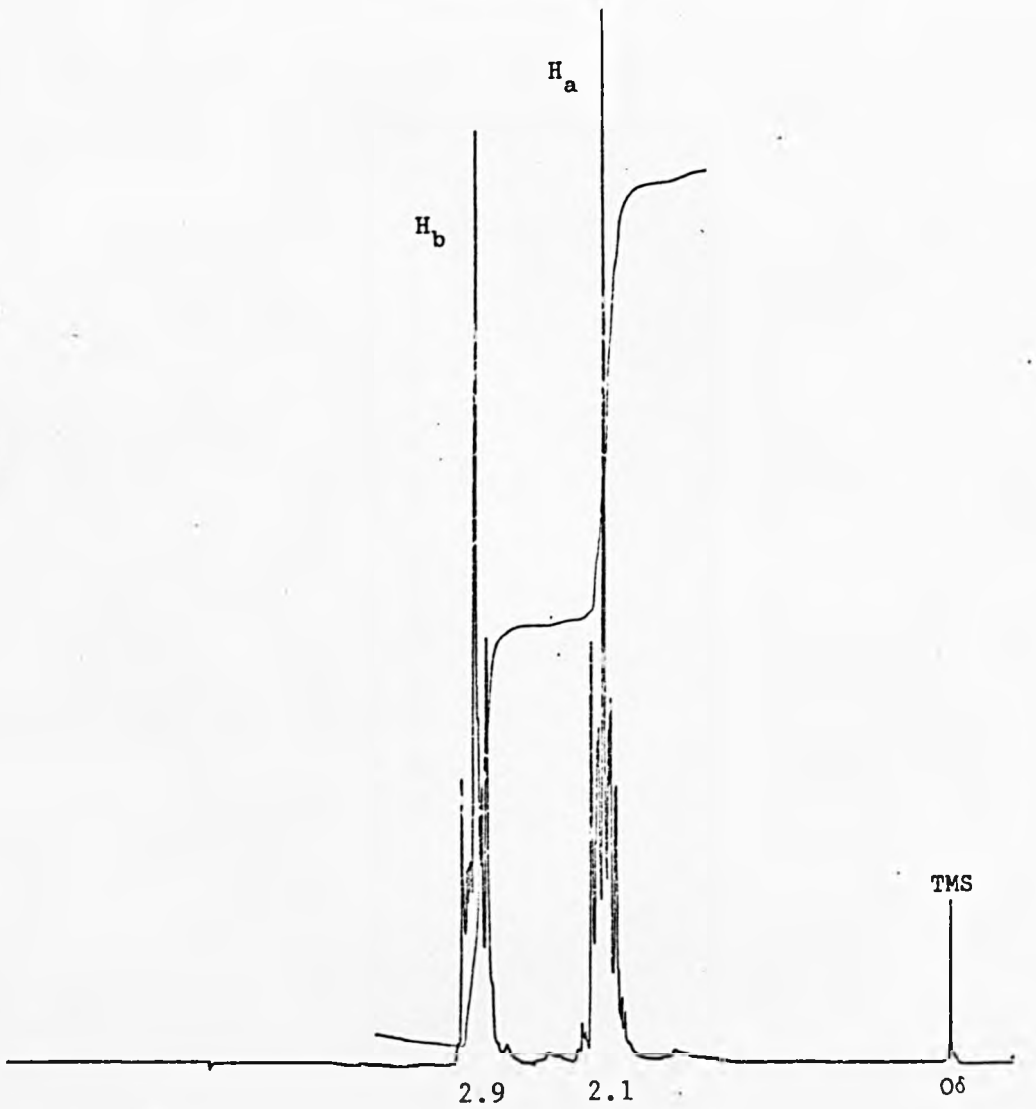


Figure 6.7. shows the p.m.r. spectrum (run in DMSO) of the product from reaction of the sulpholan dianion with hexamethylene dibromide at 223K.

FIGURE 6.7.

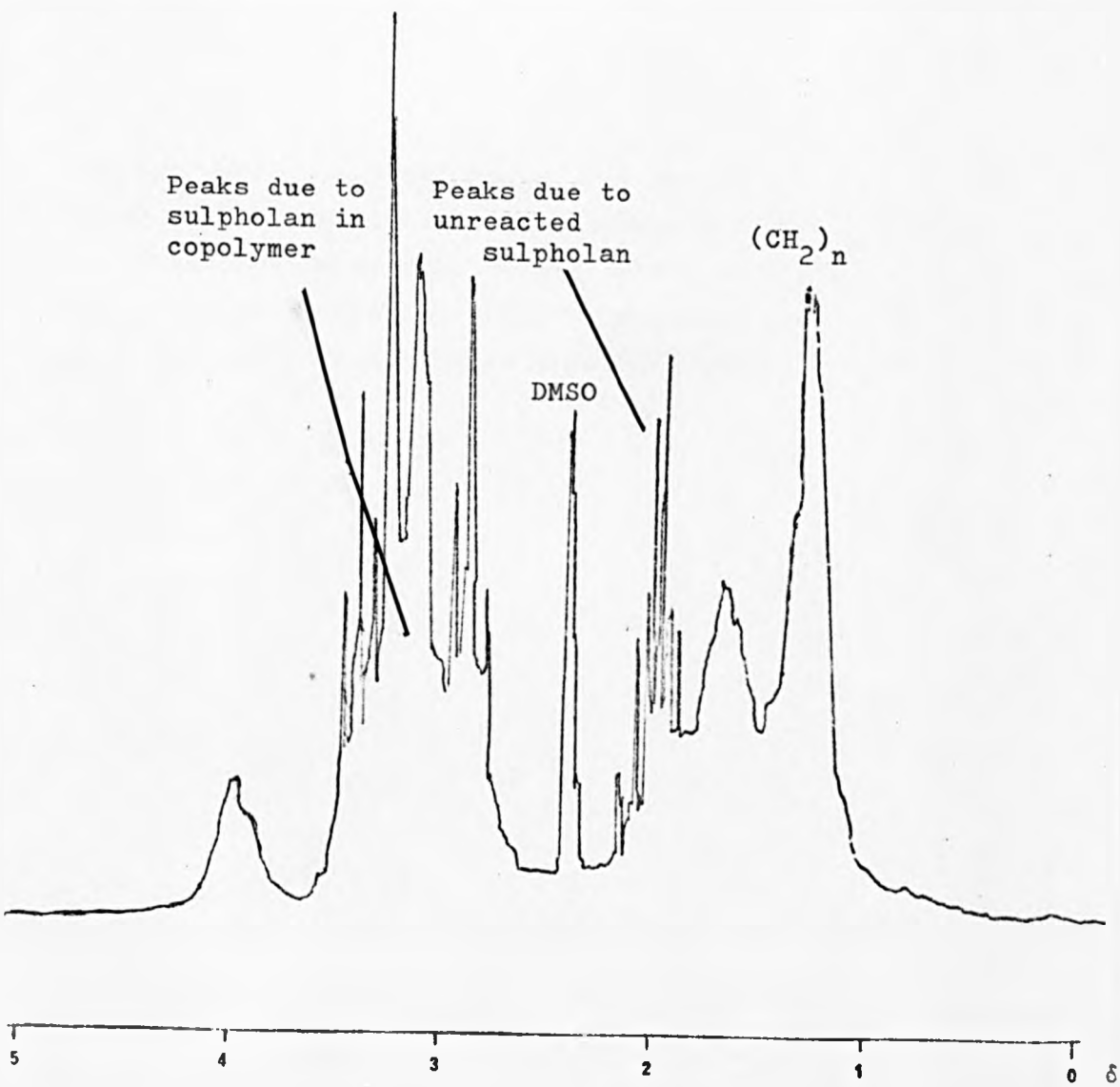

Peaks due to sulpholan in copolymer
Peaks due to unreacted sulpholan
DMSO
$(CH_2)_n$
5
4
3
2
1
0
δ

Figure 6.8. shows the p.m.r. spectrum of the product which was obtained from reaction of the sulpholan dianion with thionyl chloride at 223K. A similar spectrum was recorded when sulphuryl chloride was used.

FIGURE 6.8.

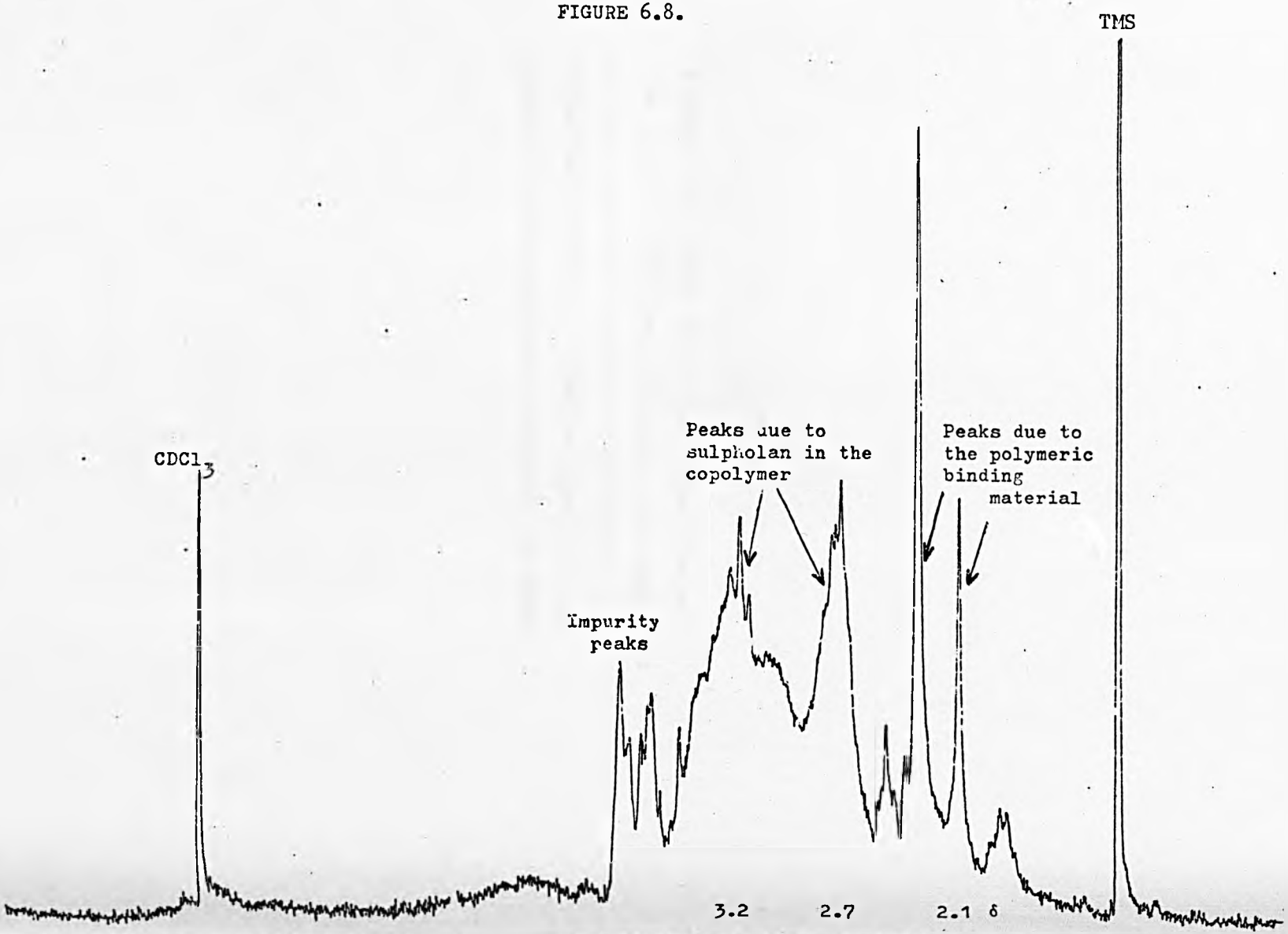

TMS
Peaks due to sulpholan in the copolymer
Peaks due to the polymeric binding material
CDCl3
Impurity peaks
3.2
2.7
2.1
δ

Figure 6.8.1. shows the p.m.r. spectrum of the reaction product from which the polymeric binding impurity had been removed.(Compare with Figure 6.8.)

FIGURE 6.8.1.

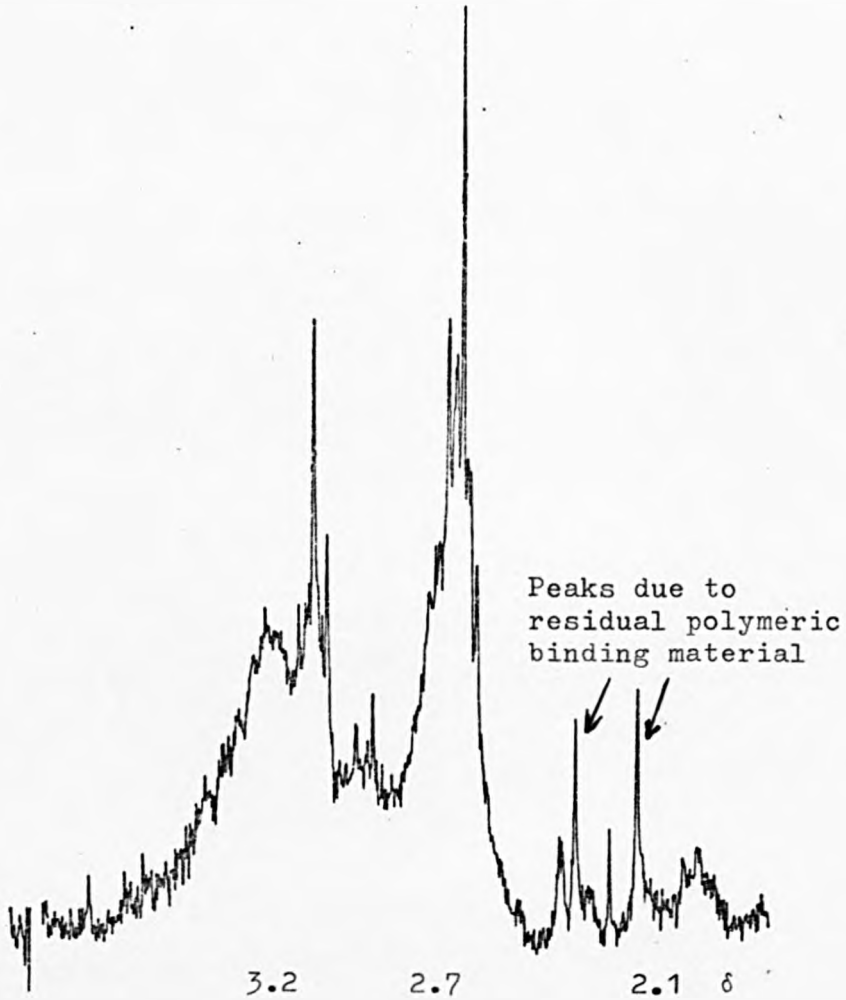


FIGURE 6.9. typical I.R. spectrum of a sulpholan copolymer

FIGURE 6.9.

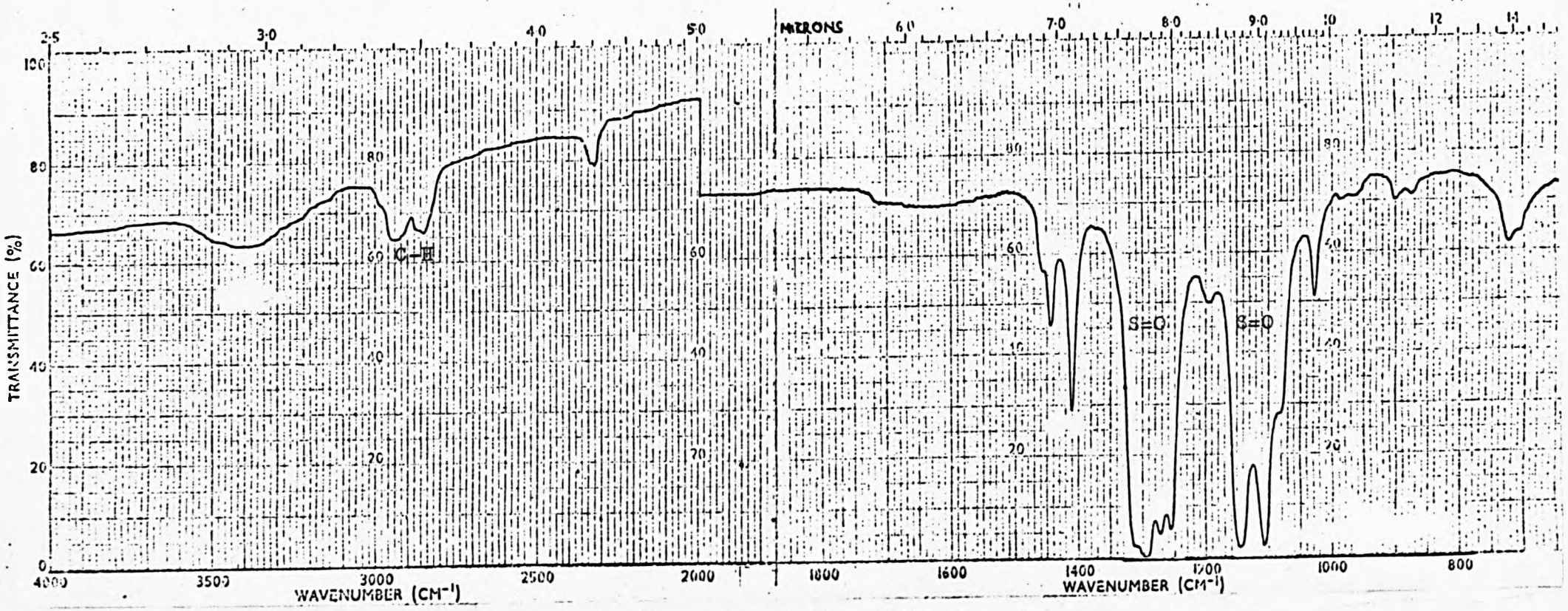

MICRONS
TRANSMITTANCE (%)
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)
C–H
S=O
S=O

Figure 6.10. shows the ^{13}C n.m.r. completely decoupled spectrum (run in D_6 Acetone) of the product from reaction of the sulpholan dianion with oxalyl chloride at 223K. Impurity peaks can be seen in the spectrum.

FIGURE 6.10.

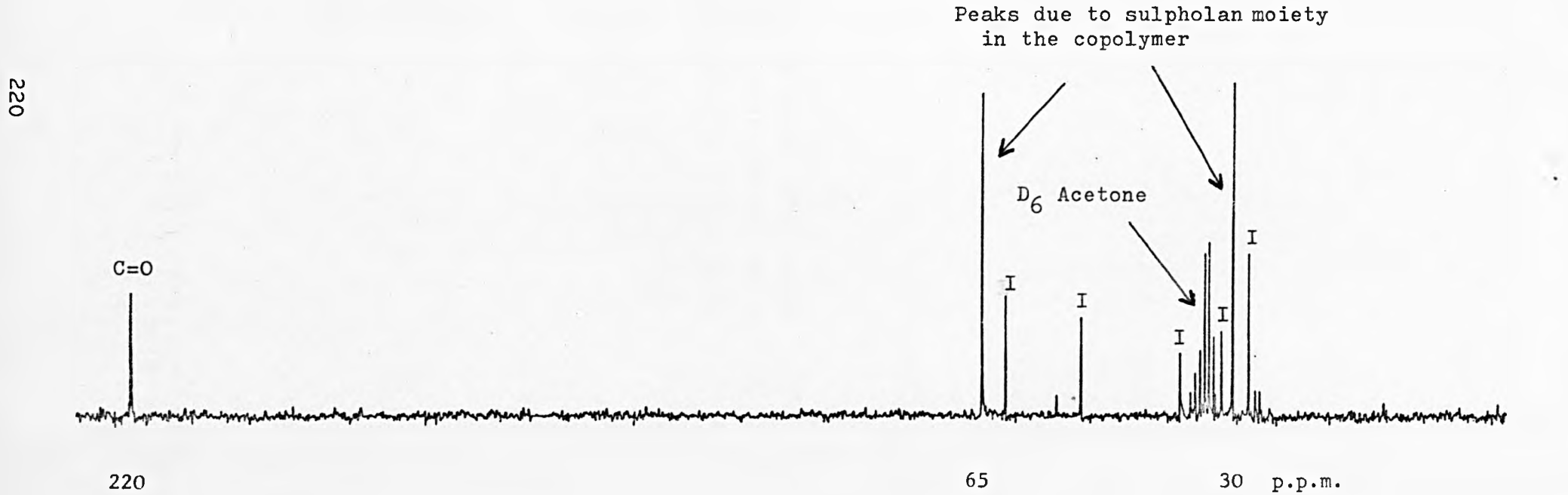

Peaks due to sulpholan moiety
in the copolymer
D6 Acetone
C=O
I
I
I
I
I
I
220
220
65
30 p.p.m.

Figure 6.11. shows the p.m.r. spectrum of the product from reaction of the sulpholan dianion with p-xylylene dibromide at 223K.

FIGURE 6.11.

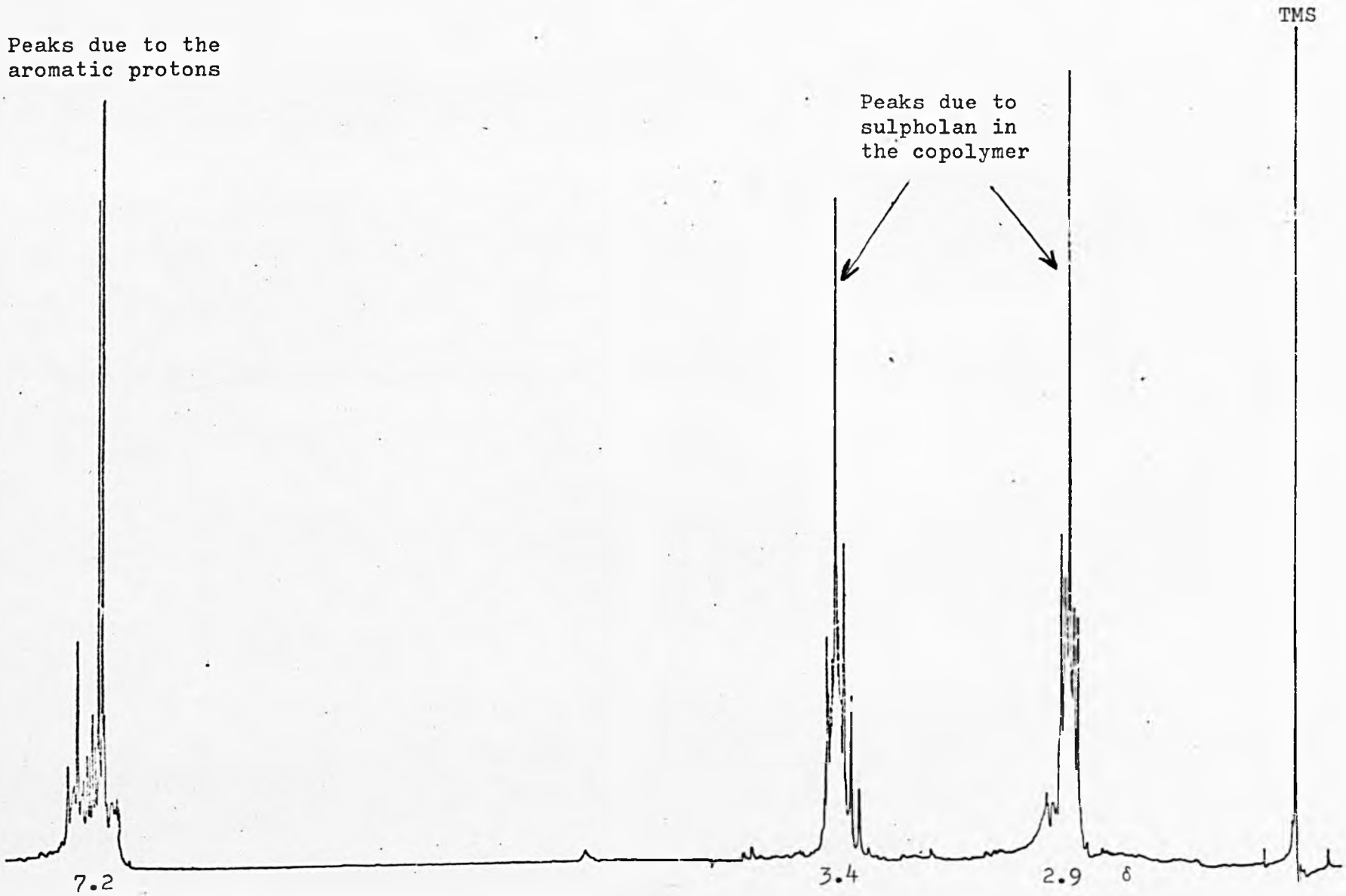

Peaks due to the aromatic protons
Peaks due to sulpholan in the copolymer
TMS
7.2
3.4
2.9
δ

Figure 6.12. shows the ^{13}C n.m.r. completely decoupled spectrum (run in D_6 Acetone) of the product from reaction of the sulpholan dianion with acetyl chloride at 223K.

FIGURE 6.12


CH3
Peaks due to sulpholan moiety
C=O
D6 Acetone
215
63
29 27
p.p.m.

FIGURE 6.13. I.R. spectra of Di-methane-sulphonyl sulpholan.

FIGURE 6.13.

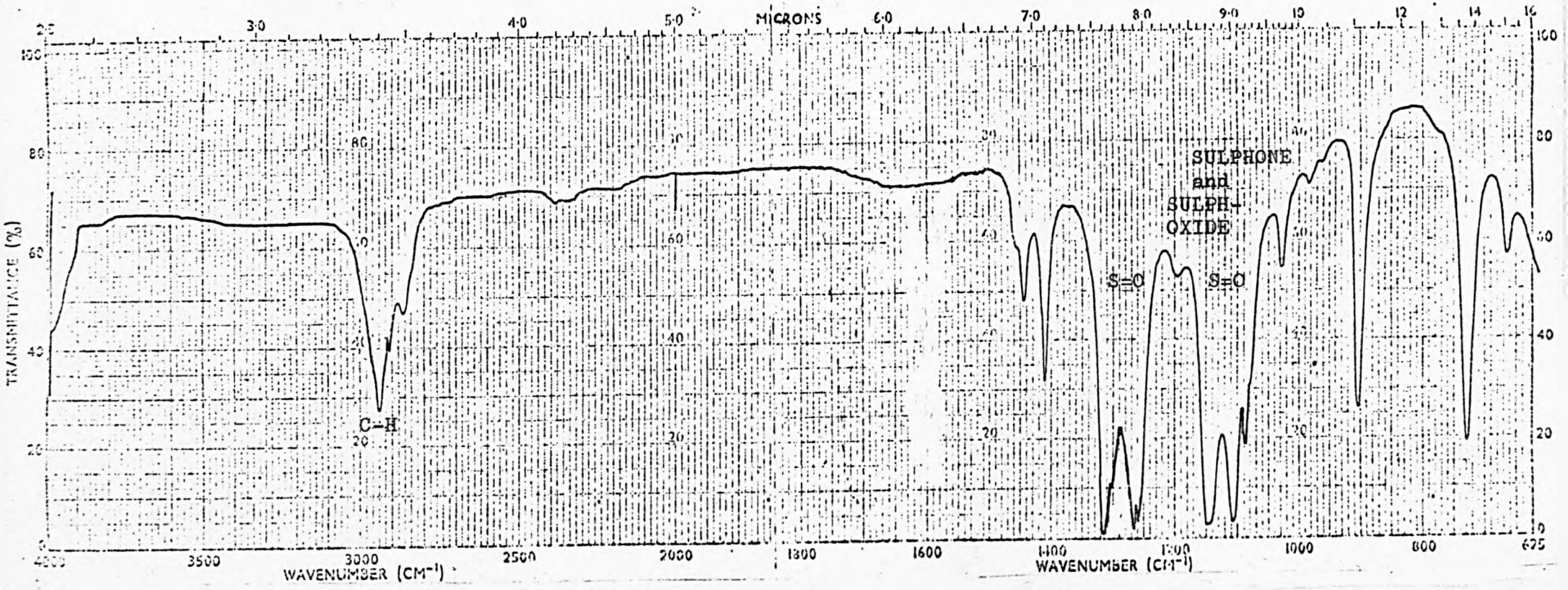
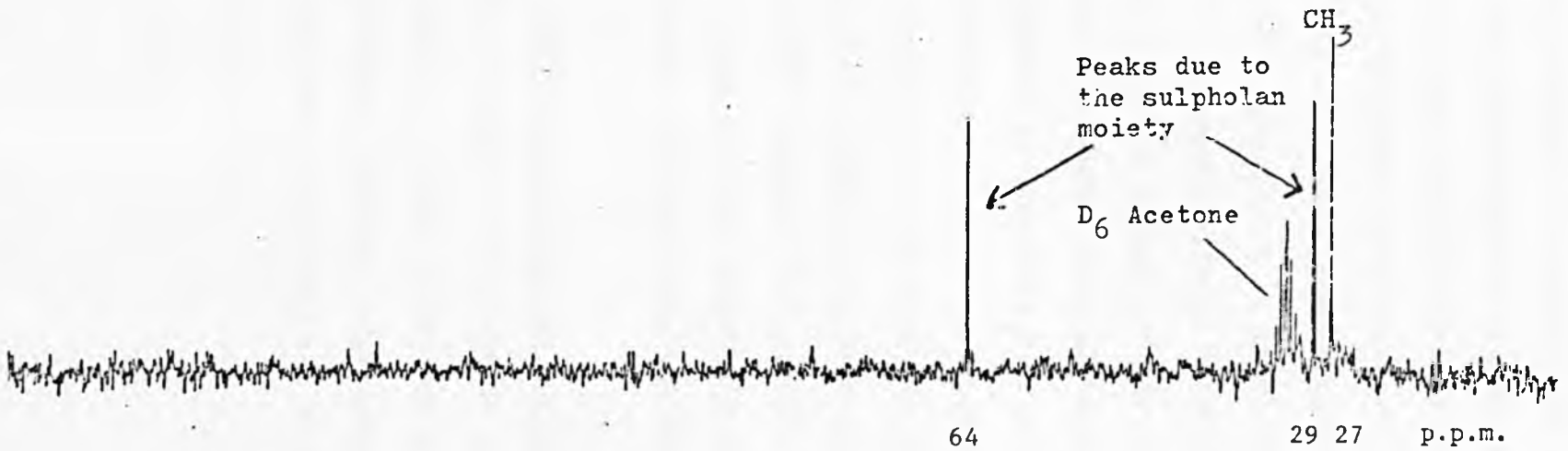

MICRONS
TRANSMITTANCE (%)
C–H
S=O
S=O
SULPHONE
and
SULPH-
OXIDE
WAVENUMBER (CM⁻¹)
WAVENUMBER (CM⁻¹)

Figure 6.14 shows the ^{13}C n.m.r. completely decoupled spectrum (run in D_6 Acetone) of the product from reaction of the sulpholan dianion with methanesulphonyl chloride at 223K.

FIGURE 6.14.



6.4. Evaluation of the Copolymers

The copolymers were prepared by a condensation procedure in which an unreactive aliphatic cyclic sulphone was incorporated in a copolymeric product. The copolymers were not as high-melting as was hoped originally; they comply with established theory that aromatic polysulphones have thermal properties superior to those of aliphatic polysulphones.

Conversion to high polymer is possibly restricted by removal of the acidic hydrogen in an anion exchange reaction which could result in a tetra-substituted sulpholan product. The desired sulpholan adduct is formed but the reactivity of the tertiary hydrogen on the carbon atom is thereby enhanced, so that it is readily removed by unreacted (a) sulpholan anions, (b) n-BuLi (equation (6.3)).

A second factor that restricts conversion to high polymer is the low solubility of the dilithio salt in hexane once a critical volume has been added to the reaction mixture. The use of butyl lithium in THF overcame this problem of precipitation (section 5.5.1.). However, this reagent is difficult to prepare, since the butyl lithium will react with the THF.

6.4.1. Evaluation of the low molecular weight sulpholan diadducts

These compounds were prepared specifically for biological testing and at the time of writing are being analysed by I.C.I. Plant Protection Division. The thietan-1,1-dioxides prepared during this study were found not to possess any significant biological activity.

6.5. Conclusions

The thietan-1,1-dioxides prepared were not susceptible to polymerisation because factors which promote polymerisation are absent. That is, no ring strain is present in these sulphones and sulphur is unavailable for reaction because it is in its highest oxidation state.

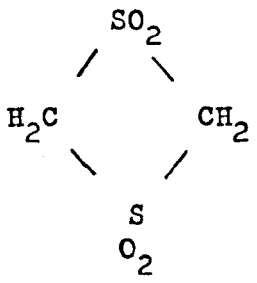
The copolymers which involved the sulpholan ring are novel, since sulpholan has never been used to form condensation copolymer, and their thermal properties resembled closely those of known aliphatic polysulphones[5,6]. (Table 6.4.).

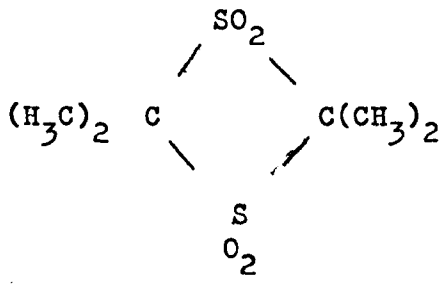
The low molecular weight sulpholan diadducts are at present unevaluated for possible biological activity. The reverse addition technique seems to have increased the purity of these products but more work is required before higher yields can be attained.

6.6. Suggestions For Further Work

Work could be continued with the copolymer systems, and with the small molecule study until a technique is perfected for obtaining high yields of pure (>95%) copolymers and of various low molecular weight adducts.

An interesting area of sulphone chemistry which has not been explored involves di-sulphone derivatives such as those shown below:





The ring strain induced by the two $-SO_2-$ groups should favour polymerisation and the linear polymers obtained from monomers of this type should possess interesting thermal properties because of the presence of the two $-SO_2-$ groups per repeat unit.

References to CHAPTER 6.

45. C. Cistaro, G. Fronza, R. Mondelli, S. Bradamante and G. Pagani, Tetrahedron Letters 1973, (5), 189.

46. A. Cerniani, G. Modena and P.E. Todesco, Gazz. Chim. Ital., 1960, 90, 382.

47. R.E. Cook, F.S. Dainton and K.J. Ivin, J. Polym. Sci., 1957, 26, 351.

48. R.M. Dodson, E.H. Jancis and G. Klose, J. Org. Chem., 1970, 35, 3520.

49. G.D. Andretti, G. Bocelli and P. Sgarabotto, Cryst. Struct. Comm., 1972, 1, 423.

50. "Handbook of Chemistry and Physics", 52nd Edit. The Chemical Rubber Co., Ohio, 1971.

51. G.L. Brode, "Chem. Sulphides Config." New York, 1968, 133.

52. W.C. Fernelius and J.E. Blanch, "Inorganic Synthesis" 1957, 5, 130.

PART C

CATIONIC POLYMERISATION OF ACENAPHTHYLENE

CHAPTER 7

INTRODUCTION

(7.1.) $$K_D = \alpha^2 c/(1-\alpha)$$

Where K_D is the dissociation constant

α is the degree of dissociation

and c is the initial concentration of salt present

(7.2.) $$SbF_6^- \rightleftharpoons SbF_5 + F^-$$

The work to be described in this section of the thesis is concerned with a kinetic study on the cationic polymerisation of acenaphthylene in nitrobenzene, by propionyl and nitronium hexafluoroantimonate and trifluoromethane sulphonic acid. It forms an extension to a study carried out in these laboratories by Mrs. M. Jones[1] on the polymerisation of acenaphthylene in dichloromethane with strong acids (H_2SO_4, $HClO_4$ and HSO_3Cl) and BF_3OEt_2.

The cationic polymerisation of acenaphthylene has been the subject of numerous investigations, under nitrogen[2] and under high vacuum conditions[3], in which different catalysts[4] and solvents[5] were employed. The polymerisations were usually followed by spectroscopic[3] or dilatometric[6] methods.

In the present work dilatometry was the primary technique used to record the polymerisation but conductimetric and spectroscopic measurements were also made during and after the polymerisation (see sections 8.2.3. and 8.2.5.).

The salts used were prepared originally by Meerwein et al.[7] and have been studied by Olah and co-workers[8-10]. However, no polymerisations have been reported in which the propionyl hexafluoroantimonate was used with nitro-solvents of high (>30) dielectric constant. The investigation was concentrated on the propionyl salt, and the fluorosulphonic acid and nitronium catalysts were incorporated in the study for comparative purposes only.

The previous kinetic investigations[2-6] had involved "classical initiator systems", BF_3OEt_2, $TiCl_4$, $SnCl_4$ etc. in the commonly used solvents dichloromethane and dichloroethane. Often for most classical systems the species which are responsible for initiation of the polymer chains cannot be identified with certainty[11]. However, the salts

(7.3.) $P_n^+ SbF_6^- \rightleftharpoons P_n^+ + SbF_6^-$

where P_n^+ is the polyacenaphthylene cation

used in this study can be regarded as "direct initiators" as they do not require the intervention of a co-catalyst, and so the initiating species is known. For a detailed discussion of the energetics involved in "direct" and "indirect" initiation Plesch's work should be consulted[11,12].

The nature of the anion is important, e.g. the effect on the DP, of which the most significant is through the effect of anion-size on K_D (equation(7.1.)). A change in the anion-size which alters α by a few per cent, will have a disproportionately large effect on the DP by changing the "paired time" with the cation, because only during this time can unimolecular decomposition of the growing ion-pair occur.

The SbF_6^- was chosen because of work by Dreyfuss et al.[13] which has shown it to be extremely stable. That is, the 1 to 2 equilibrium (equation (7.2.)) lies over on the left.

The selection of nitrobenzene as solvent for the polymerisation was made with the following theoretical and practical considerations in mind. A solvent of high dielectric constant was required to slow down the polymerisation, so that it could be followed by dilatometry. The lowering of the rate of polymerisation with increasing dielectric constant is apparently in conflict with the observation that the rates of most cationic polymerisations are greater (assuming same monomer and initiator concentrations), the more polar the solvent[14] is. It is of course invalid to compare the rates in two solvents of different polarity (even at constant concentrations of initiator and monomer), unless (1), the order with respect to monomer and initiator is the same in both solvents and (2) the concentration of active ends produced by a given concentration of initiator is the same.

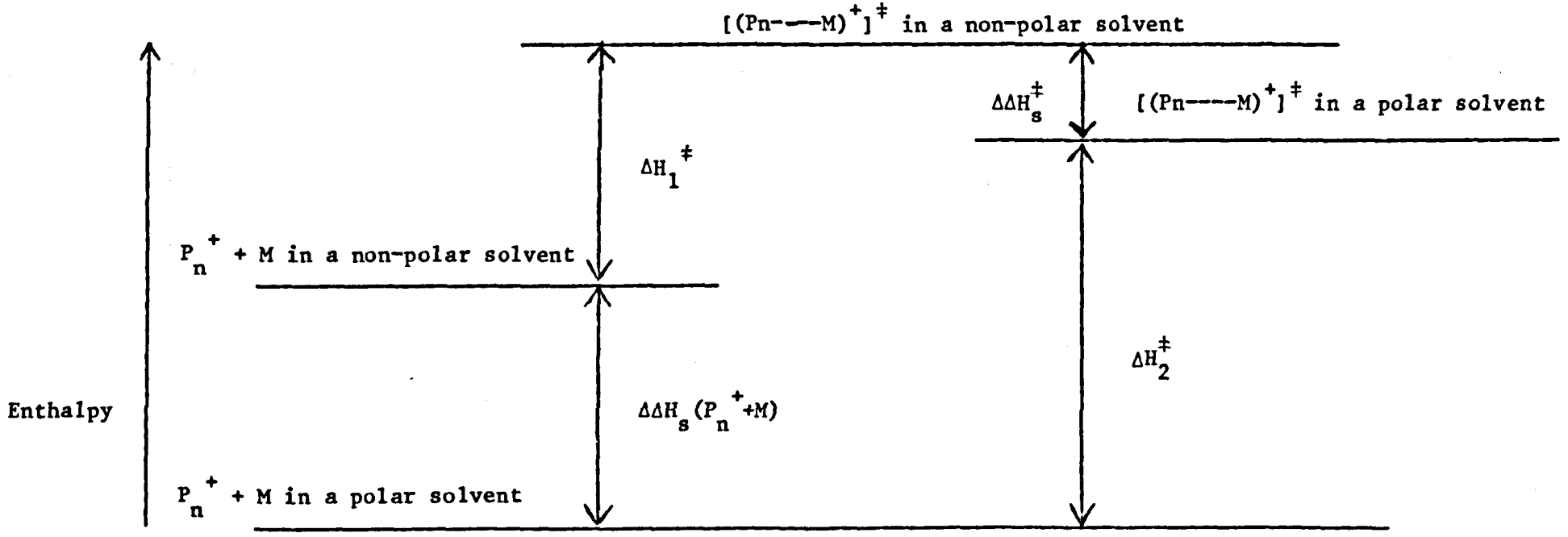
If the above criteria (1) and (2) are satisfied and if only a 1 to 2 equilibrium is involved (equation (7.3.)), the more polar a solvent, the lower are the rate constants of polymerisation of paired ($k_p^{\pm}$) and unpaired (k_p^{+}) ions. So, if higher rates are recorded in more polar solvents, a greater abundance of unpaired ions must have been present to counteract the effect which increasing dielectric constant has in reducing the rate constants of polymerisation, as long as $k_p^{\pm} > k_p^{+}$. This means that an increase in the solvent polarity must have increased the degree of dissociation (α), (equation (7.1.)) in the solvent.

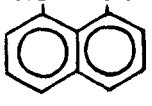
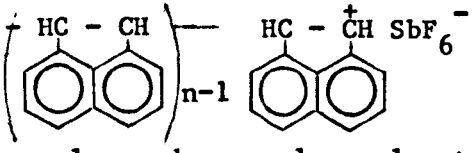
Since the addition of a polymeric cation to a monomer molecule creates a transition state which is less polar compared with the ground state, therefore, any increase in the solvent polarity will stabilize the initial state more than the transition state, and result in a higher activation energy and a lower rate constant (Figure 7.1.).

Thus, an interesting investigation was assured from the type of initiator, monomer and solvent chosen.

FIGURE 7.1. relationship of activation energy with solvent polarity.

FIGURE 7.1.



M represents the structure  and P_n^+ represents the structure 

$\Delta\Delta H_s$ is the difference between the solvation energy of $(P_n^+ + M)$ in a polar and non-polar solvent.

$\Delta\Delta H_s^{\ddagger}$ is the corresponding difference for the Transition State Complexes.

Since $\Delta\Delta H_s(P_n^+ + M) > \Delta\Delta H_s^{\ddagger}$, the activation energy $\Delta H_2^{\ddagger}$ in the polar solvent is greater than that $(\Delta H_1^{\ddagger})$ in the non-polar solvent.

References to CHAPTER 7.

1. P.H. Plesch and M. Jones, unpublished work, (Keele).
2. S. Cohen, P. Belliard and E. Maréchal, Polymer, 1973, 14, 352.
3. H.J. Prosser and R.N. Young, Europ. Polym. J., 1975, 11, 403.
4. P. Giusti, G. Puce and F. Andruzzi, Makromol. Chem., 1966, 98, 170.
5. P. Giusti, P. Cerrai, F. Andruzzi and P.L. Magagnini, Europ. Polym. J., 1971, 7, 165.
6. P. Cerrai, F. Andruzzi and P. Giusti, Makromol. Chem., 1968, 117, 128.
7. H. Meerwein, D. Delfs, and H. Morschel,Angew. Chem., 1960, 72, 927.
8. G.A. Olah, J. Amer. Chem. Soc., 1963, 85, 1328.
9. G.A. Olah, S.J. Kuhn, W.S. Tolgyesi and E.B. Baker, J. Amer. Chem. Soc., 1962, 84, 2733.
10. G.A. Olah and M.B. Comisarow, J. Amer. Chem. Soc., 1966, 88, 3317.
11. P.H. Plesch, "Cationic Polymerisation", Progress in High Polymers, Iliffe Books Ltd., London, 1968, 2, 148.
12. H. Cheradame and A. Gandini, in preparation.
13. P. Dreyfuss and J.P. Kennedy, J. Poly. Sci., 1976, Symposium No. 56, 129.
14. P.H. Plesch, Br. Polym. J., 1973, 5, 1.

CHAPTER 8

EXPERIMENTAL

8.1. Purification of Materials

Analar nitrobenzene (B.D.H. Ltd.) was recrystallised three times from itself. Approximately 40% of the initial volume was collected. This product was dried over alumina (24 hours), then it was dried and distilled under vacuum as follows: The distillation apparatus consisted of two flasks connected by a break-seal to a reservoir which was fitted with a Rotaflo tap. Nitrobenzene was kept in the reservoir, degassed and dried overnight, then distilled into the first flask which contained freshly baked alumina. The first fraction (10%) was distilled into the second flask and rejected. The middle fraction (60%) was collected in the reservoir and was sealed to the vacuum line (Figure 8.1.). The final product was slightly yellow and had $a_\kappa = 1.2 \times 10^{-8}$ μmho cm^{-1} (Lit.[15] 8×10^{-7} μmho cm^{-1}).

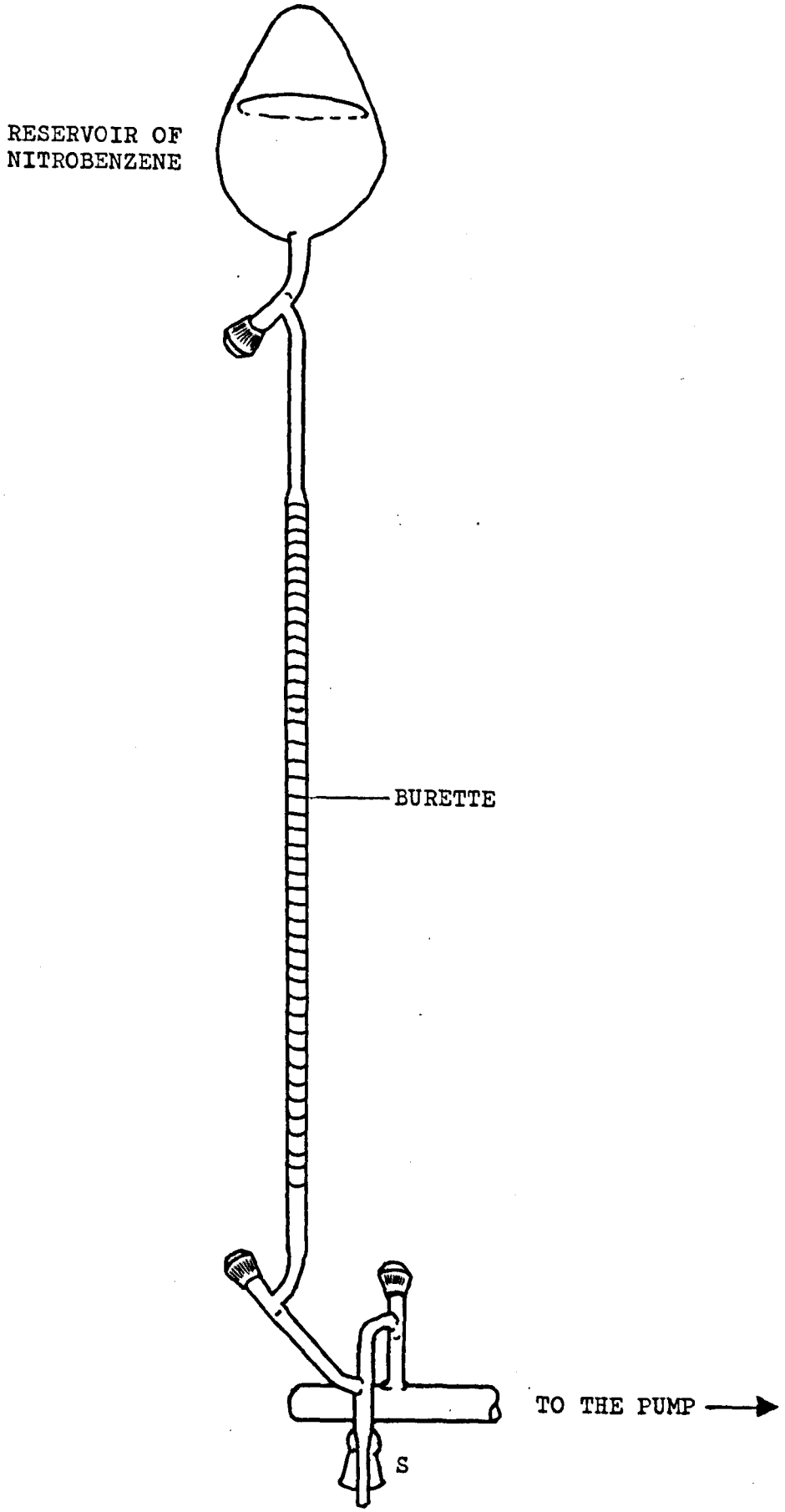
Acenaphthylene (B.D.H. Ltd.) was recrystallised from hexane and then zone refined to yield a bright yellow solid with a m.pt. 366K. (Lit.[16] 366K). The purified product was stored in black-taped bottles in the freezing compartment of a fridge, since photolysis leads to dimerisation and polymerisation[17].

The catalysts propionyl and nitronium hexafluoroantimonate were prepared in dichloromethane and nitromethane respectively by another worker, Mr. S. Pask, in Plesch's laboratories according to the method of Olah et al.[9]

Trifluoromethane sulphonic acid (B.D.H. Ltd.) was purified by a vacuum distillation before being diluted with dichloromethane and distributed into phials by the method described in section 8.2.1.

Figure 8.1. shows the nitrobenzene reservoir connected to the burette, and the special internal seal socket S.

FIGURE 8.1.



8.2. Apparatus and Experimental Methods

8.2.1. Preparation of catalyst phials

The different catalyst phials were prepared from larger phials (A), which contained about 100ml of dichloromethane solution of the catalyst. These phials (A) were incorporated in the apparatus, shown in Figure 8.2., which was then sealed to the vacuum line. Apparatus was flamed out several times during an overnight evacuation. It was sealed off under vacuum, the break-seal broken and the catalyst solution distributed into the small phials by cooling them in a dichloromethane/liquid nitrogen mush. The phials were sealed off and the concentration was found by U.V. analysis under vacuum with the apparatus shown in Figure 8.3. A phial was placed in the side tube C together with an open boat containing triphenylcarbinol (0.1g, 4×10^{-4} mole) and a magnetic breaker. The tube was then sealed off at E and the device was attached to the vacuum line at F. After pumping for the necessary time, dichloromethane (100ml) was run in and the clear solution of triphenylcarbinol was formed immediately. The apparatus was then sealed off under vacuum before the phial was broken and the U.V. absorption at 413nm[18] was measured with $1.0cm^3$ and $0.1cm^3$ silica cells. A sample calculation is given below.

Weight of phial = 1.3400g = 1.09ml of CH_2Cl_2

Total volume of solution in C = 101.09ml

Results of U.V. analysis at a constant slit width are given below.

	ABSORBANCE
1.0cm cell	1.51, 1.58 and 1.55
0.1cm cell	0.152, 0.152 and 0.153

Figure 8.2. shows the apparatus used to prepare the catalyst phials.

FIGURE 8.2.

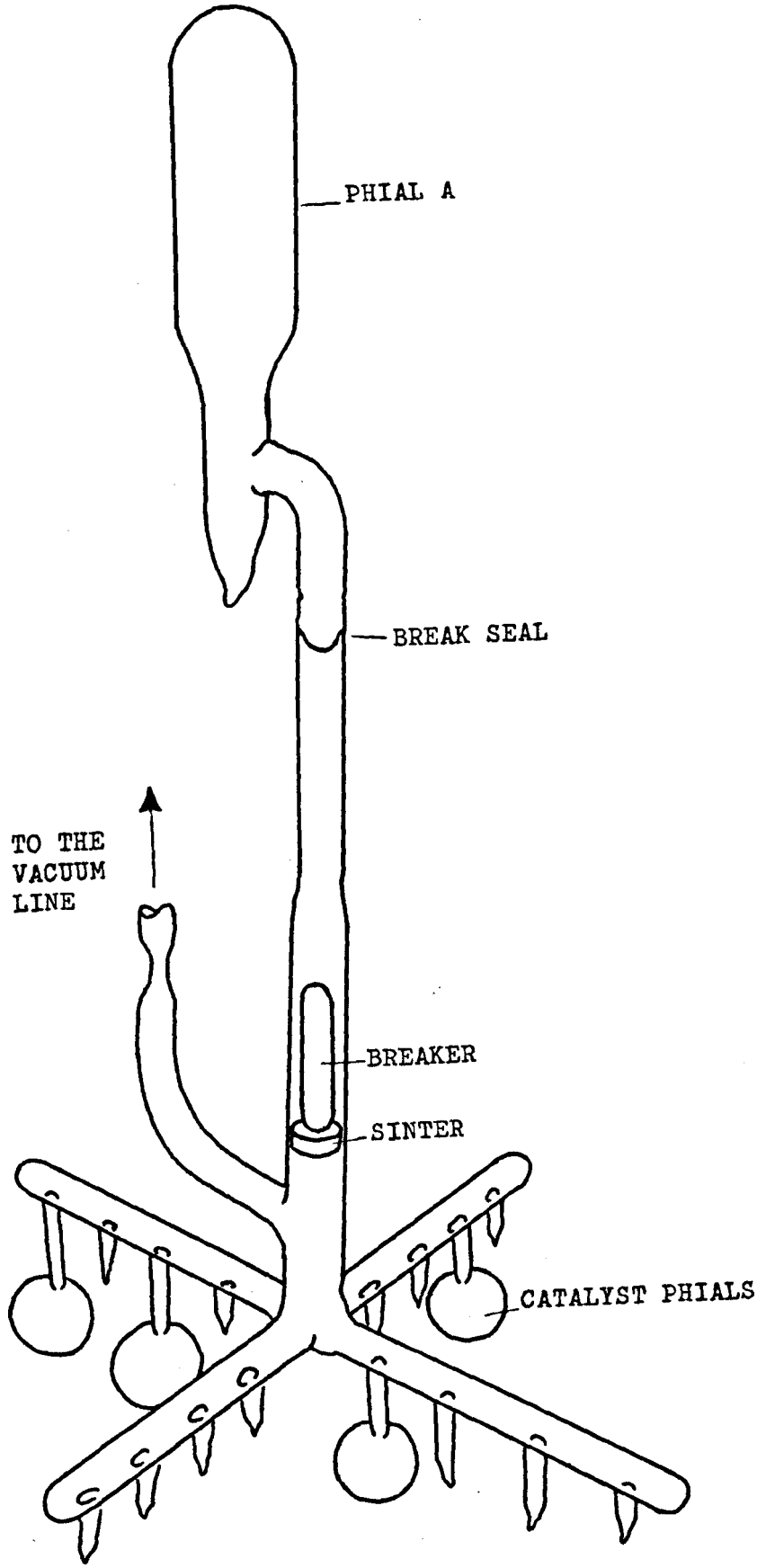
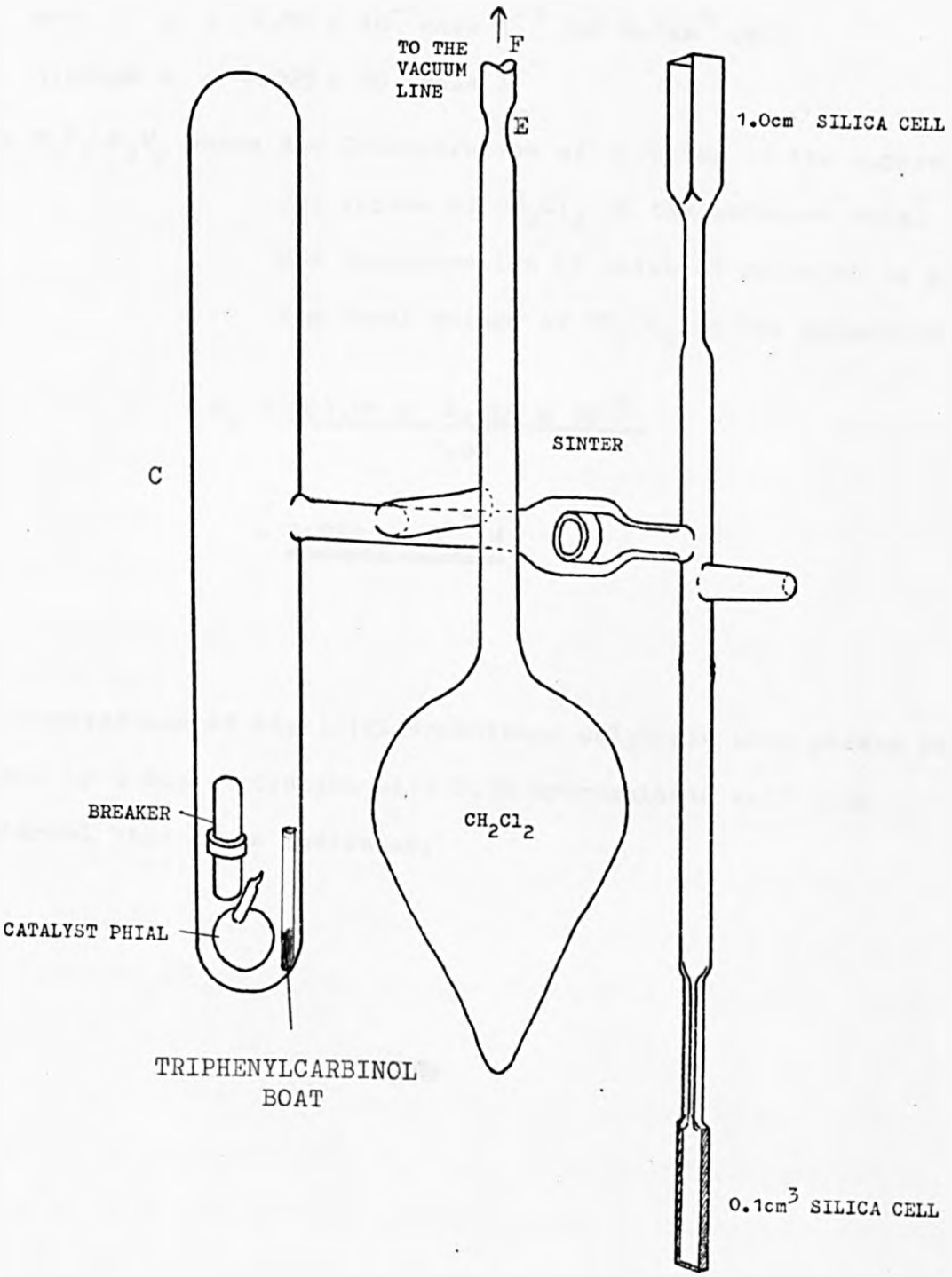

PHIAL A
BREAK SEAL
TO THE VACUUM LINE
BREAKER
SINTER
CATALYST PHIALS

Figure 8.3. shows the apparatus used to determine the concentration in the propionyl and nitronium hexafluoroantimonate phials.

FIGURE 8.3.


TO THE VACUUM LINE
F
E
1.0cm SILICA CELL
SINTER
C
BREAKER
CH_2Cl_2
CATALYST PHIAL
TRIPHENYLCARBINOL BOAT
0.1cm^3 SILICA CELL

Molar extinction coefficient (ε)for Ph_3C^+ at 413nm = 3.8± 0.1 x 10^4 l $mole^{-1}$ cm^{-1}[18].

from $c = A/\varepsilon l$

$c = 4.05 \times 10^{-5}$ mole l^{-1} for 1.0cm^3 cell

and $c = 4.00 \times 10^{-5}$ mole l^{-1} for 0.1cm^3 cell

Average $c = 4.025 \times 10^{-5}$ mole l^{-1}

From $N_1V_1=N_2V_2$ where N_1= Concentration of solution in the apparatus

V_2= Volume of CH_2Cl_2 in the catalyst phial

N_2= Concentration of catalyst solution in phial

V_1= Total volume of CH_2Cl_2 in the apparatus

$$N_2 = \frac{101.09 \times 4.025 \times 10^{-5}}{1.09}$$

$$= \underline{\underline{3.733 \times 10^{-3}\ M}}$$

The concentration of the trifluoromethane sulphonic acid phials was obtained by a back titration with 0.1M hydrochloric acid with bromothymol blue as an indicator.

8.2.2. The dilatometer and procedure for polymerisation

Polymerisation experiments were carried out in a vacuum dilatometer. The dilatometer consisted of a bulb of 5.5ml capacity with a capillary joined through a tilted side arm to a large tube (G). Attached to the tilted side arm was a conductivity cell and fused onto the large tube was a U.V. silica cell (Figure 8.4.).

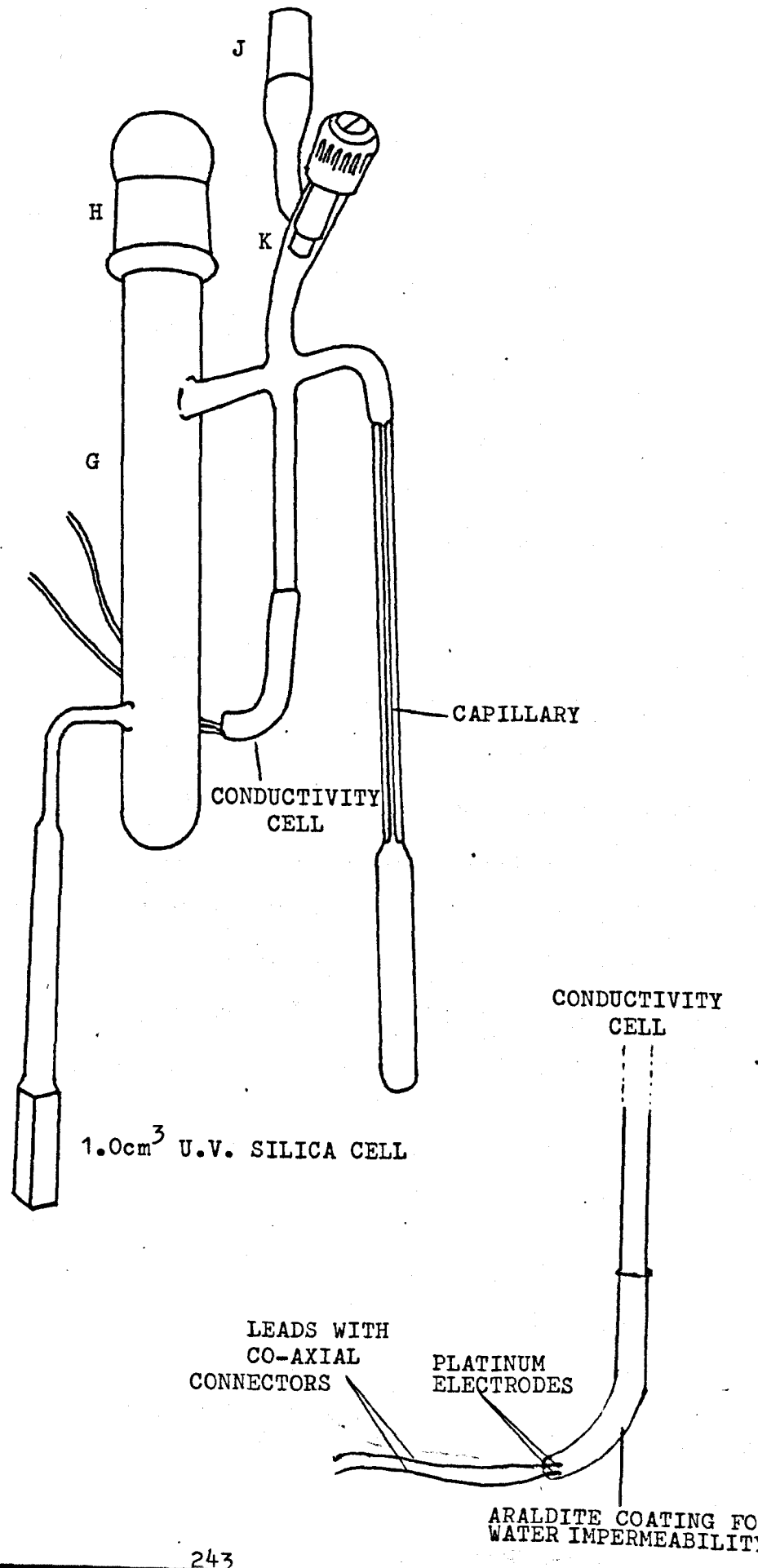
A weighed amount of monomer (0.7g, 0.23M) and catalyst phials containing approximately 1-3ml of a $10^{-3} \rightarrow 10^{-4}$M dichloromethane solution of catalyst salt were placed in G with a magnetic breaker. The joint H was sealed by Apiezon Q mastic and the apparatus was connected to the vacuum line via the black waxed joint J. The dilatometer assembly was pumped for different times because the pumping time determines the quantity of residual water; experiments were carried out in which the pumping time was altered from 1 hour to 4 hours and finally to 8 hours, in an attempt to investigate the effect of pumping time on the rate of polymerisations.

Once the necessary pumping period had been reached, nitrobenzene (20ml) was run into G from the burette. The assembly was sealed off under vacuum by closing the tap at K and was then removed from the vacuum line at J. The catalyst phial was broken by the magnetic breaker into monomer solution, and it was important to ensure that the phial was broken into all the monomer solution, otherwise the concentration of initiator would be higher than was intended.

As soon as the phial was smashed a clock was started, this allowed a check on the polymerisation time to be made accurately. A distinct colour change from yellow to green was noted in experiments with the nitronium hexafluoroantimonate initiator. No immediate

Figure 8.4. shows the dilatometer assembly used in the work.

FIGURE 8.4.


J
H
K
G
CAPILLARY
CONDUCTIVITY CELL
1.0cm3 U.V. SILICA CELL
CONDUCTIVITY CELL
LEADS WITH CO-AXIAL CONNECTORS
PLATINUM ELECTRODES
ARALDITE COATING FOR WATER IMPERMEABILITY

colour change was observed with the propionyl hexafluoroantimonate; instead, the yellow monomer solution darkened as the polymerisation proceeded. However, the acid initiator produced a deep blue colour which turned black after about 30 minutes. *

The dilatometer assembly was immersed totally in a thermostat bath (298K) after the capillary had been filled to a sufficient level for the meniscus to be followed by a cathetometer positioned outside the bath. In this way the polymerisation was followed by recording the change in meniscus height with time; readings were taken every two minutes. The meniscus generally remained stationary after about 50 minutes, but the dilatometer assembly was kept in the bath for a further 45 minutes to verify that the polymerisation had finished by checking every 15 minutes that the meniscus height had not changed.

8.2.3. Conductivity measurements

For the initial ten experiments with the propionyl salt initiator the polymerisations were followed conductimetrically by a Chandos conductivity meter which was connected to a Rikadenki chart recorder. Very little information was extracted from the conductivity measurements. The standard pattern observed was that on breaking the phial an increase in the conductivity from 0 to $\sim$0.8 μmho occurred. The conductivity remained stable around this value until the polymerisation was terminated.

* No further work was carried out with the acid catalyst because of the intractable nature of the product.

8.2.4. Variations of monomer concentrations

Six experiments with the nitronium salt initiator ($10^{-3} \rightarrow 10^{-4}$M) in which three variations of monomer concentration X,Y and Z were performed. The first, X, was the standard monomer concentration (0.23M) used with the propionyl catalyst, Y was twice that concentration and Z was half the X concentration.

Contractions of approximately 2.6cm were normal if the concentration of monomer was 0.23M. The contractions stayed the same when twice the monomer concentration was employed, and in these experiments residual monomer was detected by the procedure outlined in section 8.2.5.

8.2.5. U.V. analysis

Once a steady cathetometer reading was obtained i.e. when the polymerisation had finished, the U.V. cell on the side arm G was filled with the polymer solution and placed in the spectrometer. The spectrum of the terminal carbenium ion over the range 390-850nm was recorded, with nitrobenzene as the reference solvent. This gives $[P_n^+]$.

Another U.V. method for determining the $[P_n^+]$ was devised by Pask and Plesch[19]. The technique involved the reaction of 1,1-diphenylethylene with the "living" polymer solution, and utilized the resultant strong absorption due to the 1,1-diphenylethylene cations for the detection of very low active end concentrations.

A known volume of 1,1-diphenylethylene was added to the reaction mixture by the following procedure: Excess of 1,1-diphenylethylene solution was poured on top of the Rotaflo tap (Figure 8.4.) and the

tap was slightly opened to suck it in. The tap was then closed once the required volume of 1,1-diphenylethylene solution had entered the dilatometer. The excess 1,1-diphenylethylene on top of the tap was discarded. The polymer solution was mixed thoroughly before the U.V. spectrum of the 1,1-diphenylethylene terminated polyacenaphthylene was recorded. By this technique no large volume of air was introduced into the dilatometer assembly.

The concentration of active ends was determined from both experiments and compared with the initiator concentration used. Values which were obtained from this analysis for the various polymerisations are listed in Table 9.3.

Because the monomer is soluble in alcohol the presence of any unreacted monomer was investigated by U.V. analysis on the alcohol solution obtained from the precipitation of the polymer. The method involved the preparation of a standard 0.23M monomer solution in nitrobenzene. One ml of this was diluted with absolute ethanol to give a 1.2×10^{-5}M solution, the U.V. spectrum of which was recorded. The alcoholic solution (1ml) obtained from precipitation of the polyacenaphthylene was diluted in an identical manner to the standard monomer solution. Comparison of the absorbance recorded for the solution of the standard with that for the polymer solution gave the residual concentration of monomer.

8.3. Isolation Procedure

Methylated spirits was used to terminate the polymerisations by the same method described for end capping with 1,1-diphenylethylene (section 8.2.5.). The polymer solution was then precipitated in an excess of methylated spirits and was then steam distilled for four hours to remove the nitrobenzene. It was important to remove nitrobenzene from the precipitated polymers because residual traces would effect the vapour pressure osmometry molecular weight determinations and the spectroscopic end group investigations.

When trifluoromethane sulphonic acid was the initiator used, the precipitated polymer was a black charcoal-like solid, which was not investigated further.

Although many of the polymeric mixtures were steam distilled twice, a faint odour of nitrobenzene was detectable from the light brown polyacenaphthylenes. Therefore, other techniques for extraction of nitrobenzene were carried out. (a) Soxhlet extraction (b) a distillation procedure with tertiary butanol and (c) a distillation procedure with trichloroethylene, (b) and (c) were performed on polymer samples which had been previously steam distilled. These solvents were used because (1) tertiary butanol being more polar should displace nitrobenzene from the polymers and (2) trichloroethylene avoids the formation of a two-phase system present with tertiary butanol.

The Soxhlet extraction with water was inferior compared with the steam distillation method for removing nitrobenzene from precipitated polymers.

The distillations with either tertiary butanol or trichloroethylene proved to be successful, in that both yielded solids that had no smell of nitrobenzene unlike the products from the Soxhlet extraction which smelt heavily of nitrobenzene.

8.3.1. Molecular weight determinations

Vapour pressure osmometry and gel permeation chromatography were used to measure the molecular weights, and by the latter technique the molecular weight distributions (DPD) were also obtained.

Vapour pressure osmometry was used to determine the molecular weights of a few polyacenaphtylene samples, and these were also run on the g.p.c., which gave the "polystyrene equivalent molecular weight" ($\bar{M}n$).

In this way a calibration of the g.p.c. columns for polyacenaphthylene was made and the molecular weight of each polymer was then found from the g.p.c. and this calibration.

Discussion of the g.p.c. traces is given in Chapter 9.

8.4. End Group Analysis

Purified polymers were submitted for I.R., U.V. and ^{13}C n.m.r. analysis to determine the structure of the end groups and the presence of any 1,8 C=C units (the reason for examining the polymers for these C=C bonds will be explained in Chapter 9).

I.R. spectra of acenaphthene, acenaphthylene and polyacenaphthylene were recorded in carbon tetrachloride (for the monomers) and in chloroform (for the polymer). Bromine was then added to the acenaphthylene and polyacenaphthylene solutions and the I.R. spectra were obtained. A comparison of the different spectra which were recorded, and the bands which disappeared after bromination was then carried out.

Quantitative infra-red analyses were performed on isolated polyacenaphthylenes to reveal spectroscopically the presence of carbonyl and nitronium moieties which arise from the propionyl and nitronium initiators respectively. No peaks were recorded at the wavenumbers expected for carbonyl (1680-1820cm^{-1}) and nitronium (1550cm^{-1} region) absorptions.

The U.V. spectra of a high and low molecular weight polyacenaphthylene, acenaphthylene and acenaphthene were obtained. The absorption bands present in each spectrum were compared.

The ^{13}C spectra of acenaphthylene and polyacenaphthylene were recorded in deuterated chloroform. Concentrated sulphuric acid was then added carefully to the deuterated chloroform solution of polymer and the spectra recorded.

A full discussion of all the results obtained from the spectroscopic analyses is given in Chapter 9.

8.5. Analytical Techniques

8.5.1. U.V. spectroscopy

This analytical method was employed for, (a) determining the concentration of the catalyst solutions, (b) determining the residual monomer concentration after polymerisation, (c) determining the active-end concentration, (d) to record the various absorption bands of a polymerisation mixture with different initiators and (e) to detect the presence of (1,8-C=C) units in the isolated polymers.

The investigation of (a) was carried out with an SP 500 Unicam U.V. spectrophotometer.

The spectra obtained in the studies (b), (c), (d) and (e) were recorded on a Perkin Elmer 402 U.V. spectrophotometer and a Pye Unicam SP8-100 ultraviolet spectrophotometer.

8.5.2. ^{13}C magnetic resonance

This technique was used in the end-group analysis of the polyacenaphthylenes.

The spectra were recorded on a J.E.O.L. JNM, FX100 spectrometer, in deuterated solvents , and with tetramethylsilane as the internal standard.

References to CHAPTER 8.

15. J. Pac, M.Sc. Thesis, Keele, 1966.

16. P.H. Plesch and V. Bertoli, "U.V. Atlas of Organic Compounds", 3, Butterworths, London, 1967.

17. Private communication from R.N, Young.

18. V. Bertoli, Ph.D. Thesis, Keele, 1967.

19. S. Pask and P.H. Plesch, unpublished results, (Keele).

CHAPTER 9

RESULTS AND DISCUSSION

9.1. Results Section

Although only a brief kinetic study on the polymerisation of acenaphthylene was carried out because of time limitations, it is possible to draw some conclusions from the work and these will be discussed later in this chapter.

9.1.1. Kinetic results

The kinetic data were analysed in terms of zero, first and second order equations, but the only satisfactory straight line was obtained from the first order plot according to equation (9.1.).

$$-dm/dt = k_1 m \qquad (9.1.)$$

Where k_1 is the first order rate constant

and m is the monomer concentration

This procedure was used for the first two experiments, the subsequent experiments were treated by a computer programme utilizing the Moore method[20].

The polymerisation was followed by dilatometry, so the change in m with time can be recorded by the change in the height of meniscus in the dilatometer. Figure 9.1. shows a typical computer trace which was obtained for a first order plot according to equation (9.2.); the slope gives the k_1 value for the polymerisation.

$$\log [(h_o - h_\infty)/(h_t - h_\infty)] \quad \text{vs. time} \qquad (9.2.)$$

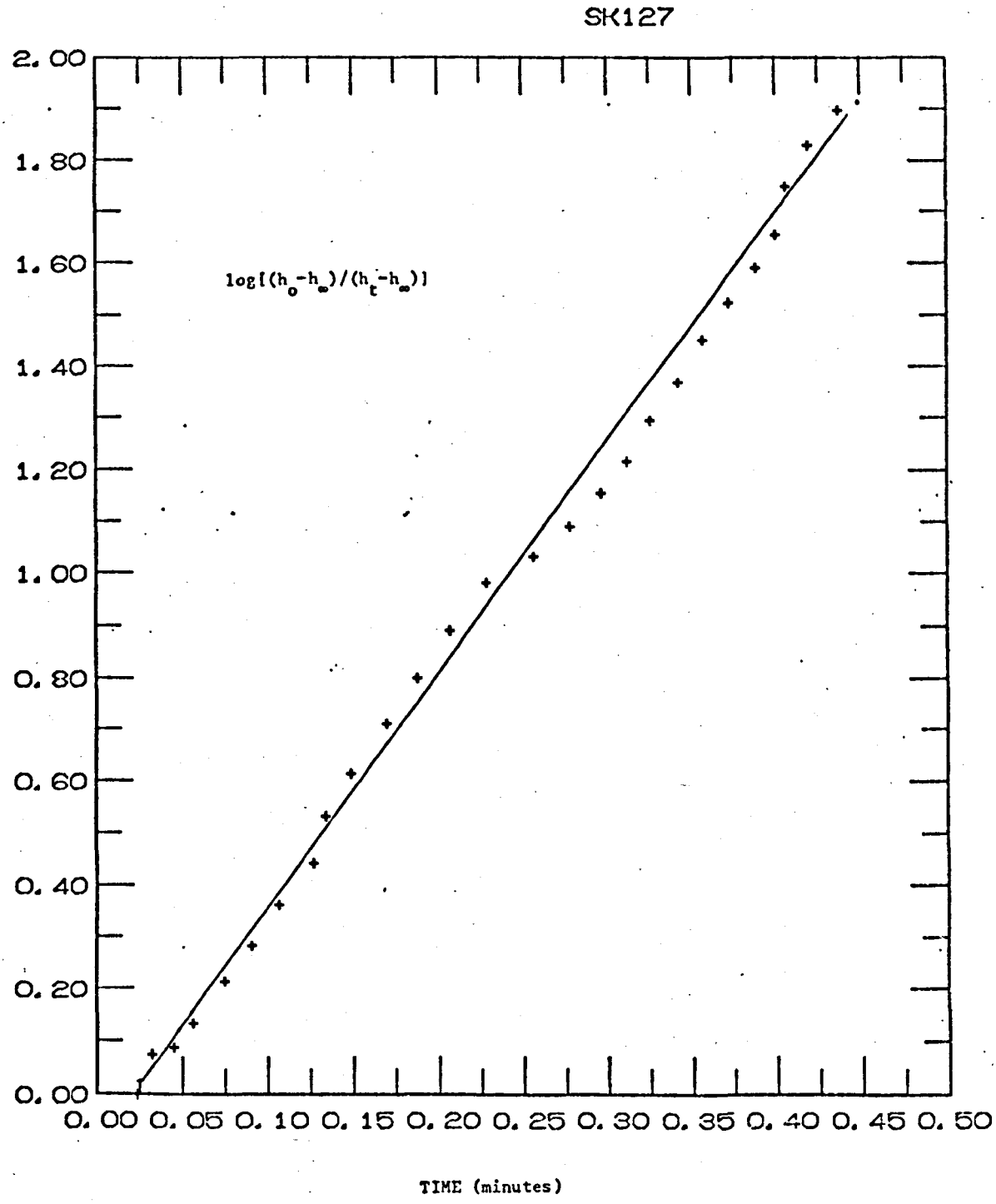
Where h_o = initial reading

h_t = reading at time t

and h_∞ = reading at infinity

FIGURE 9.1. a typical first order computer plot of the dilatometer readings vs. time

FIGURE 9.1.



XAXIS; SCALE = X * (10 ** -4)

YAXIS; SCALE = Y * (10 ** 0)

The linear plot which was obtained indicates that the polymerisation was of first order with respect to monomer.

Tables 9.1. and 9.2. list the kinetic data which are utilized in the following discussion.

The effect of different pumping times on the k_1 values (section 8.2.2.) can be seen from Figure 9.2. The points of the lines II to IV lay on straight lines (within experimental uncertainty) above an initiator concentration (c) of about $5x10^{-4}M$, but below this value the points deviate from the straight lines.

Higher rates are recorded for longer pumping times, which means that more impurities are removed, the longer the system is pumped. This argument applies up until some value of time when the removal of impurities is so slow and the pumping times so long as to render the exercise pointless.

The intercept of the lines II to IV is a measure of the concentration of impurities present and it can be seen that the intercept ($0.3x10^{-4}M$) of line IV is closer to the origin than that for line II (the 1 hour plot) ($2.1x10^{-4}M$). The difference between these intercepts ($1.8x10^{-4}M$) is a realistic figure for the quantity of impurities present in the system. No polymerisations were carried out with catalyst concentrations $<2.0x10^{-4}M$, because the small difference between c and the concentration of impurities would lead to the "killing" of most of the initiator and would be difficult to reproduce from one experiment to another.

Point A is interesting because it was one of the few polymerisations carried out at low c. But without further work in this region it is difficult to decide whether the curvature towards point A is significant or if it is an effect of c approaching the concentration of impurities present in the system.

TABLE 9.1

KINETIC DATA OBTAINED FROM POLYMERISATIONS WITH THE PROPIONYL HEXAFLUOROANTIMONATE INITIATOR.

Experiment No.	m/(mole ℓ^{-1})	10^4 c/ (mole ℓ^{-1})	Pumping Time/h	10^4 k_1/s^{-1}
SK139	0.23	13.72	1.0	18.26
141	0.23	9.20	1.0	11.05
140	0.23	6.28	1.0	6.17
142	0.23	5.70	1.0	5.80
143	0.23	3.80	1.0	4.36
146	0.23	3.40	4.0	6.90
128	0.23	5.35	4.0	6.41
121	0.23	9.80	4.0	17.63
127	0.23	6.50	4.0	7.60
124	0.23	14.30	4.0	10.04
122	0.23	6.38	4.0	8.80
123	0.23	8.19	4.0	10.16
125	0.23	3.79	4.0	2.30
145	0.23	2.20	8.0	8.50
130	0.23	3.20	8.0	7.93
134	0.23	4.36	8.0	8.88
136	0.23	9.5	8.0	16.20
138	0.23	5.60	8.0	9.60
131	0.23	8.20	8.0	11.74
144	0.23	5.91	8.0	9.11
137	0.23	6.70	8.0	10.32
132	0.23	7.40	8.0	11.67
135	0.23	9.66	8.0	14.33

TABLE 9.2

KINETIC DATA OBTAINED FROM POLYMERISATIONS WITH THE NITRONIUM HEXAFLUOROANTIMONATE INITIATOR.

Experiment No.	m/(mole ℓ^{-1})	10^4 c/ (mole ℓ^{-1})	Pumping Time/h	k_1/s^{-1}
SK151	0.115	5.85	8	8.8
152	0.115	7.2	8	13.21
153	0.46	10.3	8	9.1
154	0.46	5.2	8	9.9
155	0.23	9.35	8	15.3
156	0.23	8.5	8	12.5

Figure 9.2. shows the plots of k_1 vs. c at constant m (0.23M), which were obtained for different pumping times before initiation by the propionyl hexafluoroantimonate catalyst (10^{-3}-10^{-4}M).

FIGURE 9.2.

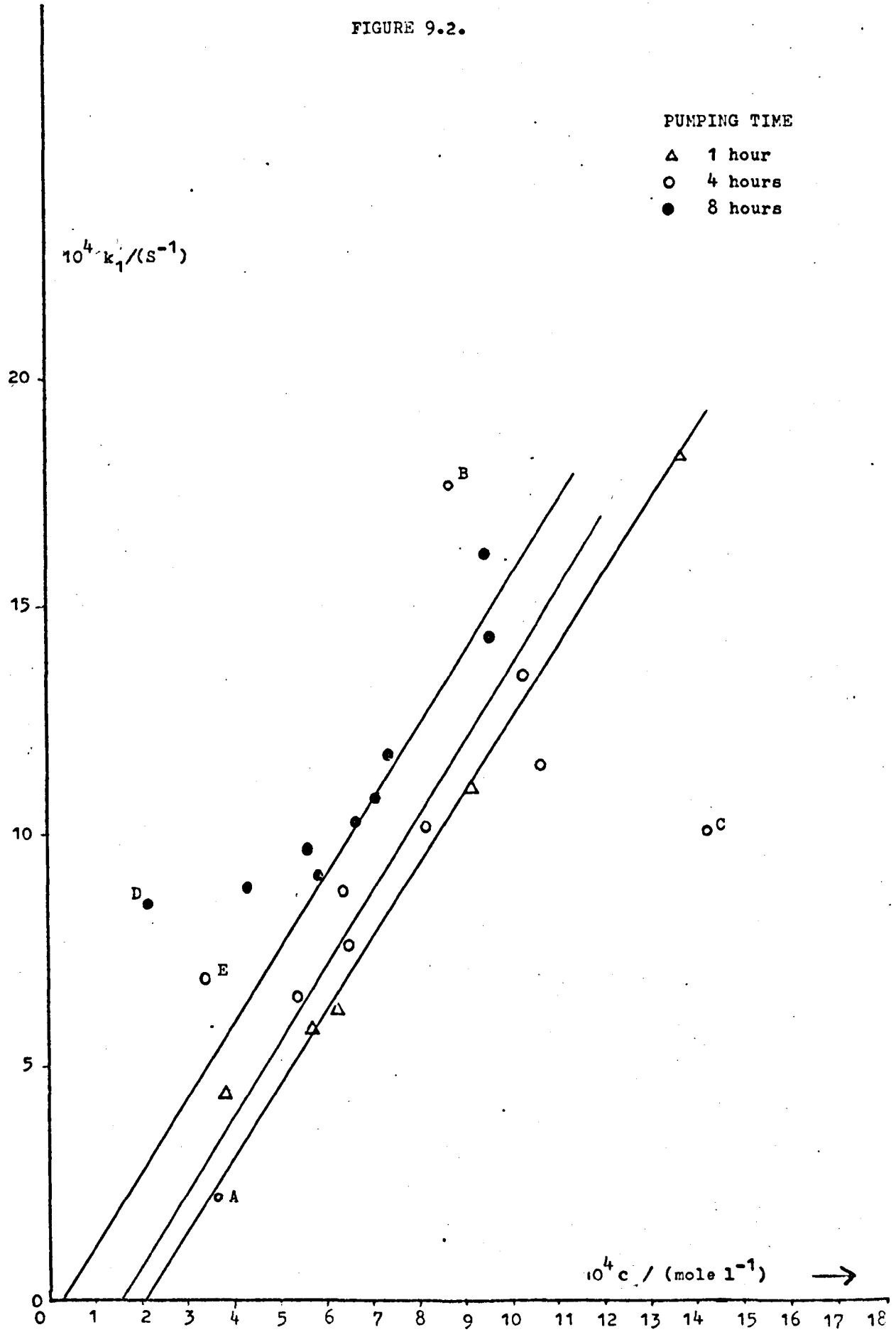
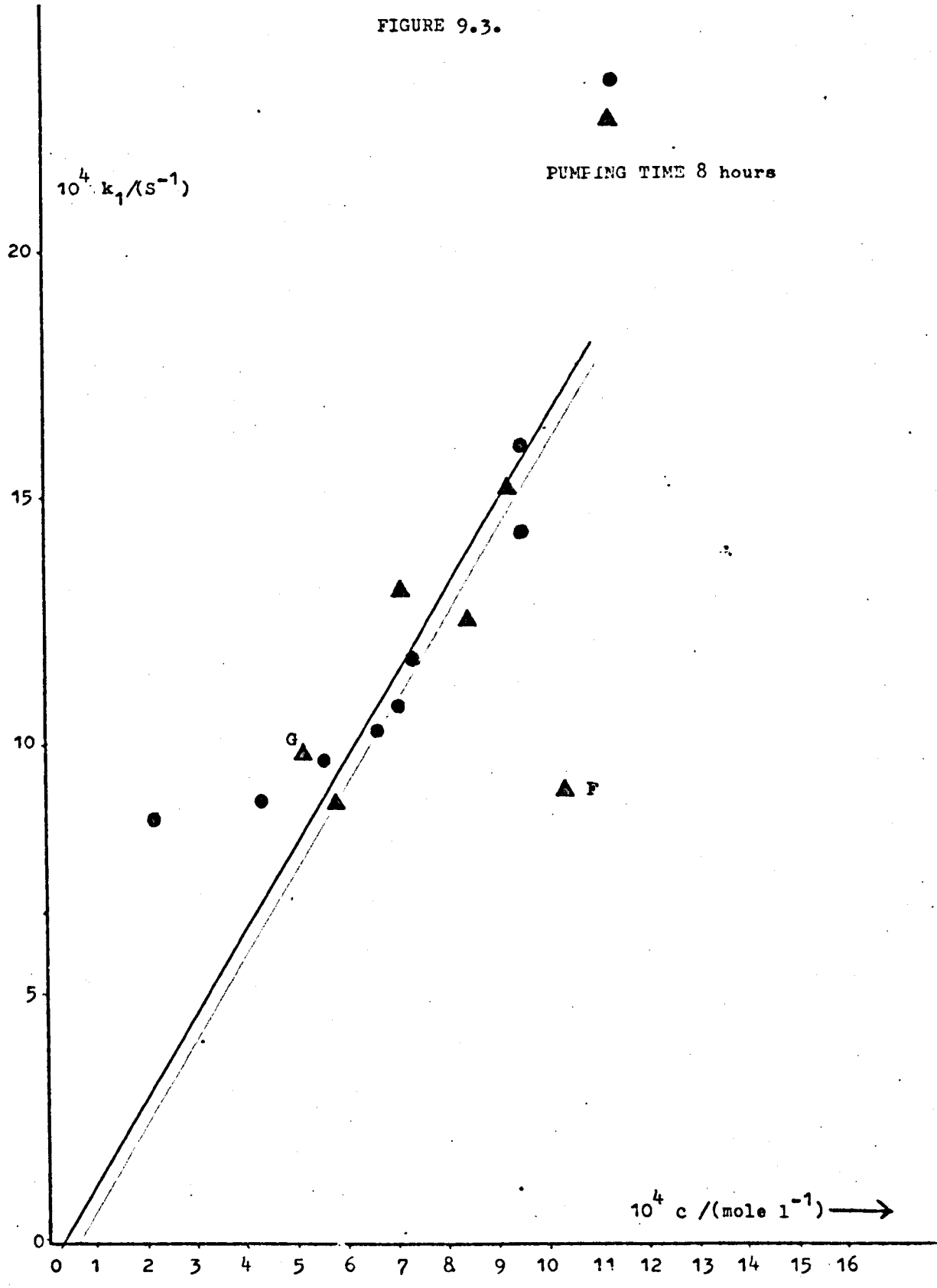

PUMPING TIME
1 hour
4 hours
8 hours
$10^4 k_1'/(s^{-1})$
20
15
10
5
0
A
B
C
D
E
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18
$10^4 c$ / (mole l^{-1})

Figure 9.3. shows the plots of k_1 vs. c after 8 hours pumping before initiation with the propionyl and nitronium hexafluoroantimonate (10^{-3}-10^{-4}M). A constant m (0.23M) was used for polymerisations with the propionyl salt but m was varied (0.115-0.46M) with the nitronium salt.

FIGURE 9.3.


PUMPING TIME 8 hours
$10^4 k_1/(s^{-1})$
20
15
10
5
0
G
F
10^4 c /(mole l^{-1})
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16

Points B and C were derived from the first series of experiments undertaken and are suspect since the author was at that time inexperienced in the operation of a vacuum line and unfamiliar with the technique of dilatometry.

Points D and E were obtained from polymerisations for which a dichloromethane solution of acenaphthylene was prepared in the dilatometer. The solution was then pumped (to remove the dichloromethane) for a stipulated period before addition of the nitrobenzene and the standard experiment was completed. The reason for the dichloromethane solution procedure was to investigate whether higher rates of polymerisation would be observed, as a consequence of the water present dissolving in dichloromethane and so being removed more rapidly when the system was pumped. These results do indicate that this procedure did have some beneficial effect.

Figure 9.3. shows the plot of k_1 vs. c for polymerisations initiated by the nitronium salt. The line of best fit (V) has an intercept which is almost the same (0.3×10^{-4}M) as that for the "8 hour" plot (line IV, reproduced here) with the propionyl salt. It is clear that within the experimental uncertainty line IV is as good a fit for the results obtained with the nitronium salt as line V.

Points F and G are suspect and will be disregarded in further calculations because they were derived from the polymerisations in which 40% residual monomer was found by U.V. analysis (see section 9.1.2.).

9.1.2. Results of U.V. analysis of the polymerisation mixture

The U.V. analysis to determine the residual monomer concentration was carried out on the alcoholic solution obtained from precipitation of the polymer (section 8.2.5.). In all polymerisation mixtures initiated by the propionyl salt no residual monomer was detected. That is, the peak at 350nm in the U.V. spectrum of the monomer was not found in the U.V. spectrum of the polymer (see section 9.1.4.). This means that the upper limit of residual m in the polymer solution can be estimated to be 5% from conventional assessment of the errors by a method which is given in the Appendix.

However, 40% of residual monomer was found in the two polymerisations initiated by the nitronium salt in which m was 0.46M, i.e. twice the standard m used for the other polymerisations. Since the monomer used for these polymerisations was purified a long time previous to performing the experiment the anomaly may be accounted for by a higher concentration of impurities being present, which may lead to termination of the growing chains. A single broad intense absorption at 445nm was recorded for the $[P_nAN^+]$ of a polymerisation initiated by the propionyl salt. Addition of 1,1-diphenylethylene to this polymerisation mixture had no effect on the peak position but an approximately ten-fold increase in intensity was observed.

A peak of identical shape and intensity to the absorption recorded at 445nm was obtained at 465nm in the U.V. spectrum of the $[P_nAN^+]$ for a polymerisation initiated by the nitronium salt. The absorptions at 465nm and 445nm were not present in the U.V. spectrum of the monomer. However, also present in the U.V. spectrum of this $[P_nAN^+]$ were peaks at 675nm and 575nm (Table 9.3.). The peak at 575nm grew steadily at the expense of the peak at 675nm, until the initial

TABLE 9.3

U.V. ANALYSIS OF THE ACENAPHTHYLENE POLYMERISATION MIXTURE.

Initiator System	$[P_nAN^+]$	$[P_nCH_2CPh_2^+]$
$NO_2^+SbF_6^-$	675nm	631nm
	575nm	590nm
	465nm	442nm
$CH_3CH_2CO^+SbF_6^-$	445nm	445nm

ratio of the peak heights had been reversed after 1.5 hours. Addition of 1,1-diphenylethylene to these polymerisation mixtures moved the absorptions to 631nm, 590nm and 442nm, and the intensity of the peak at 442nm was approximately ten times that of the peak at 465nm.

Young and Prosser[3] have studied spectroscopically the polymerisation of acenaphthylene by $TiCl_4$ and they observed the appearance of absorptions at 565 and 730nm and assigned the peak at 565nm to the acenaphthylene carbenium ion (λ_{max} 560nm in H_2SO_4)[3]. The origin of the peaks (575 and 675nm) and the reason for their appearance is discussed in section 9.2. In an earlier investigation Young[21] studied the U.V. spectrum of the acenaphthylenium ion in 98% H_2SO_4 and found peaks were also present at 305nm, 410nm, 430nm and 635nm. The value for the molar extinction coefficient at 430nm recorded in this early study was used in the calculation of the active end concentration $[P_n^+]$ (equation (9.3.)).

The $[P_n^+]$ was calculated from the U.V. absorptions due to (a) the terminal carbenium ions (P_nAN^+) and (b) the terminal 1,1-diphenylethylene carbenium ions ($P_nCH_2CPh_2^+$) (section 8.2.5.). A sample calculation is given below:

From the Beer Lambert Law $c = A/\varepsilon l$ (9.3.)

with $\varepsilon_{430} = 3.5 \times 10^3\ M^{-1}cm^{-1}$ for $[P_nAN^+]$ ref 21

$\varepsilon_{430} = 3.9 \times 10^4\ M^{-1}cm^{-1}$ for $[P_nCH_2CPh_2^+]$ ref 18

and the measurements were carried out in a 1.0cm cell so l in equation (9.3.)is equal to 1.0.

For the $[P_nAN^+]$ experiment (SK 140)

$$c = 1.68/3.5 \times 10^3$$

$$\underline{c = 4.8 \times 10^{-4} M}$$

and for $[P_nCH_2CPh_2^+]$ experiment A is 17.6*

so $c = 17.6/3.9\times10^{4}$

$$\underline{c = 4.5\times10^{-4}M}$$

C_o is defined as the initial catalyst concentration.

The c_o used in this experiment (SK140)=6.28×10^{-4}M. Thus, the $[P_nAN^+]$ was $0.8c_o$ and the $[P_nCH_2CPh_2^+]$ was $0.75c_o$.

These values were obtained consistently throughout the work (Table 9.4.).

Figure 9.4. shows the graphs of $[P_nAN^+]$ and $[P_nCH_2CPh_2^+]$ against c_o; both are straight line plots passing through the origin. Discussion of the conclusions which can be drawn from these plots is given in section 9.2.

The concentration of the species which are responsible for the peaks at 575nm and 675nm can only be estimated, since the values used are those for absorptions at 560nm and 635nm:

From equation (9.3.) $c = A/\varepsilon l$

with $\varepsilon_{560} = 5.4\times10^{4}\ M^{-1}\ cm^{-1}$ ref 21

$\varepsilon_{635} = 9.2\times10^{4}\ M^{-1}\ cm^{-1}$ ref 21

and (a) Absorbance for peak at 575nm after 1.5 hours = 0.88

(b) Absorbance for peak at 675nm after 1.5 hours = 0.40

$l = 1.0cm$

(a) $c = 0.88/5.4\times10^{4} \times 1$

$$\underline{c = 1.6\times10^{-5}M}$$

(b) $c = 0.4/9.2\times10^{4} \times 1$

$$\underline{c = 4.3\times10^{-6}M}$$

* The absorbance was recorded with a "mask" over the U.V. light beam, which reduced the intensity by a factor of ten.

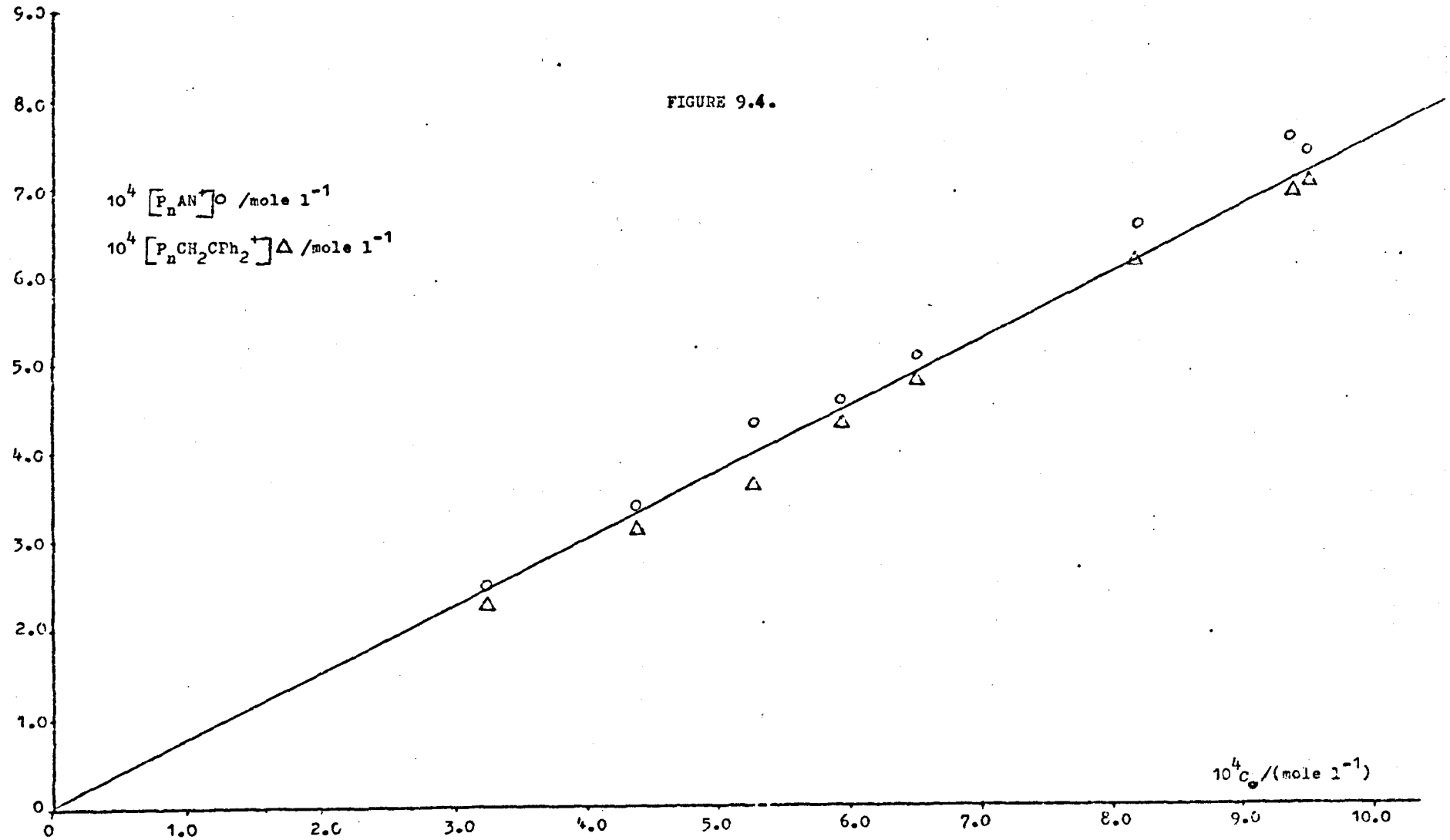
TABLE 9.4

RESULTS OBTAINED FOR THE ACTIVE-END CONCENTRATIONS.

Experiment No.	10^4 c/ (mole ℓ^{-1})	10^4 $[P_nAN^+]$/ (mole ℓ^{-1})	$10^4[P_nCH_2CPh_2^+]$/ (mole ℓ^{-1})	$[P_nAN^+]/c_o$	$[P_nCH_2CPh_2^+]/c_o$
SK127	6.50	5.11	4.76	0.79	0.73
128	5.35	4.09	3.92	0.76	0.73
130	3.20	2.48	2.25	0.78	0.70
131	8.20	6.51	6.03	0.79	0.74
134	4.36	3.31	3.19	0.76	0.73
136	9.5	7.39	7.01	0.78	0.74
151	5.85	4.53	4.29	0.77	0.73
154	5.20	4.34	3.57	0.83	0.69
155	9.35	7.55	6.89	0.81	0.74

Figure 9.4. shows the common plot for the calculated [P_nAN^+] and [$P_nCH_2CPh_2^+$] data vs. c_o for polymerisations which were initiated by the propionyl and nitronium hexafluoroantimonate.

FIGURE 9.4.


10^4 [P_nAN^+]o /mole l^{-1}
10^4 [$P_nCH_2CPh_2^+$]Δ /mole l^{-1}
$10^4 c_o$/(mole l^{-1})
0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
9.0
10.0

These concentrations are inaccurate because of the assumption made concerning the ε values, but they indicate the order of magnitude of the concentration of the products which absorb at 575nm and 675nm and so it can be concluded that there is about $0.1c_o$ of unknown species present in the nitronium system after 1.5 hours.

9.1.3. Results of DPD measurements

The g.p.c. traces (Figures 9.5. and 9.6.) of the polyacenaphthylenes indicate very broad molecular weight distributions, and show an extremely intense U.V. signal, which was to be expected from consideration of the aromatic content in the polymers. The U.V. detector has in fact been saturated as evinced by the non-symmetry of the U.V. peak.

The strong U.V. signal and corresponding D.R. signal at the exclusion limit (count 19) of the g.p.c. columns are not significant, since it is in this region that the impurities show up which are held on the columns, from previous g.p.c. runs, and become dislodged from the pores. These impurities may give misleading intensities for the U.V. and D.R. signals. No calibration of the g.p.c. columns is valid in this region because of the drastic departure from linearity. Therefore, the idea that the peak at count 19 is due to nitrobenzene or unreacted monomer cannot be confirmed or refuted without further experimentation.

A summary of the M.W. values obtained from g.p.c. and vapour pressure osmometry (v.p.o.) measurements is given in Table 9.5. and their significance is discussed in section 9.2.

TYPICAL G.P.C. TRACES OBTAINED FOR THE POLYACENAPHTHYLENE

FIGURE 9.5. SK140

FIGURE 9.6. SK127

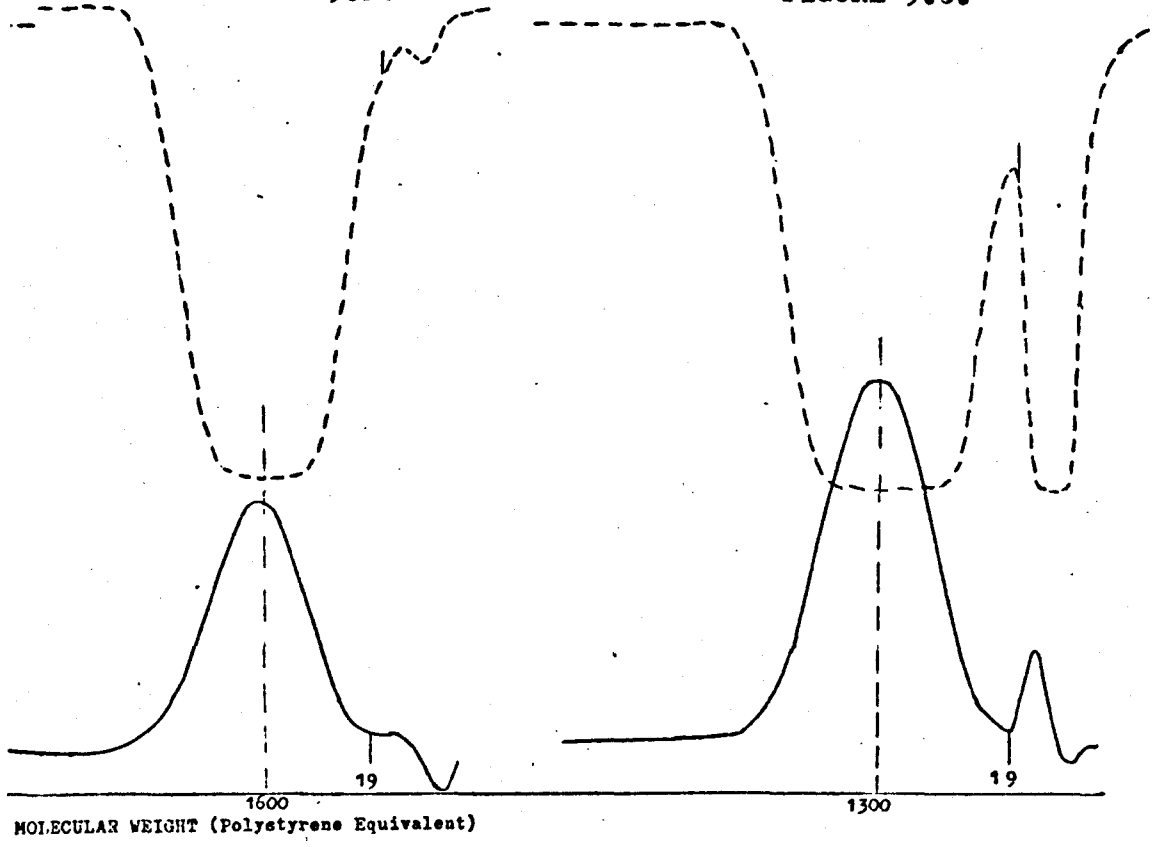


TABLE 9.5

SOME TYPICAL MOLECULAR WEIGHTS OF POLYACENAPHTHYLENES OBTAINED BY G.P.C. AND V.P.O. MEASUREMENTS.

Expt. No.	G.P.C.*	V.P.O.
SK127	1300	1000
130	1200	1000
132	1000	850
140	1600	1400
141	1500	1400
146	1100	900
135	1100	
139	1100	
142	1100	
143	1100	
128	1000	
121	1200	
124	1300	
122	1200	
123	1100	
125	1000	
145	1000	
134	1100	
136	1200	
138	1200	
131	1200	
144	1000	
137	1000	

* Polystyrene Equivalent Mn values.

9.1.4. Results of the end-group analysis

Figures 9.7., 9.8, and 9.10 show, respectively, the I.R., ^{13}C N.M.R., and U.V. spectra which were aimed at the analysis for terminal (1,8 C=C) unsaturation.

The infra-red study was intended only to verify that the (1,8 C=C) unsaturated moieties were present.

The infra-red spectra of acenaphthylene and acenaphthene were compared in an attempt to assign the absorptions due to the (1,8 C=C) unsaturation. The absorptions from the aromatic C=C and (1,8 C=C) unsaturation in both systems is in the 1600-1400cm^{-1} region: addition of bromine to the acenaphthylene solution reduced the intensity of the peaks at 910cm^{-1}, 1460cm^{-1}, 1475cm^{-1} and removed the "definition" on the C-H stretching bonds in the 3080cm^{-1} region. The bromination procedure was repeated with polyacenaphthylene and tended to remove the fine splitting on the absorptions (Figure 9.7.).

The infra-red technique demonstrated some changes on addition of bromine, but no confirmation that only specific bromination across the (1,8 C=C) bonds had occurred was possible from this method of analysis.

The ^{13}C N.M.R. technique was then used to (i) detect the presence of the (1,8 C=C), (ii) to clarify the situation which occurred when reagents were added to remove all unsaturation.

Completely decoupled (COM) and off-resonance spectra were recorded. A COM spectrum exhibits all the separate carbon absorptions, whereas an off-resonance spectrum records the couplings each carbon has with another.

Trace (a) in Figure 9.8. is a COM spectrum of acenaphthylene and shows seven absorptions, which indicates that there are seven

FIGURE 9.7. SPECTRA OBTAINED DURING I.R. ANALYSIS

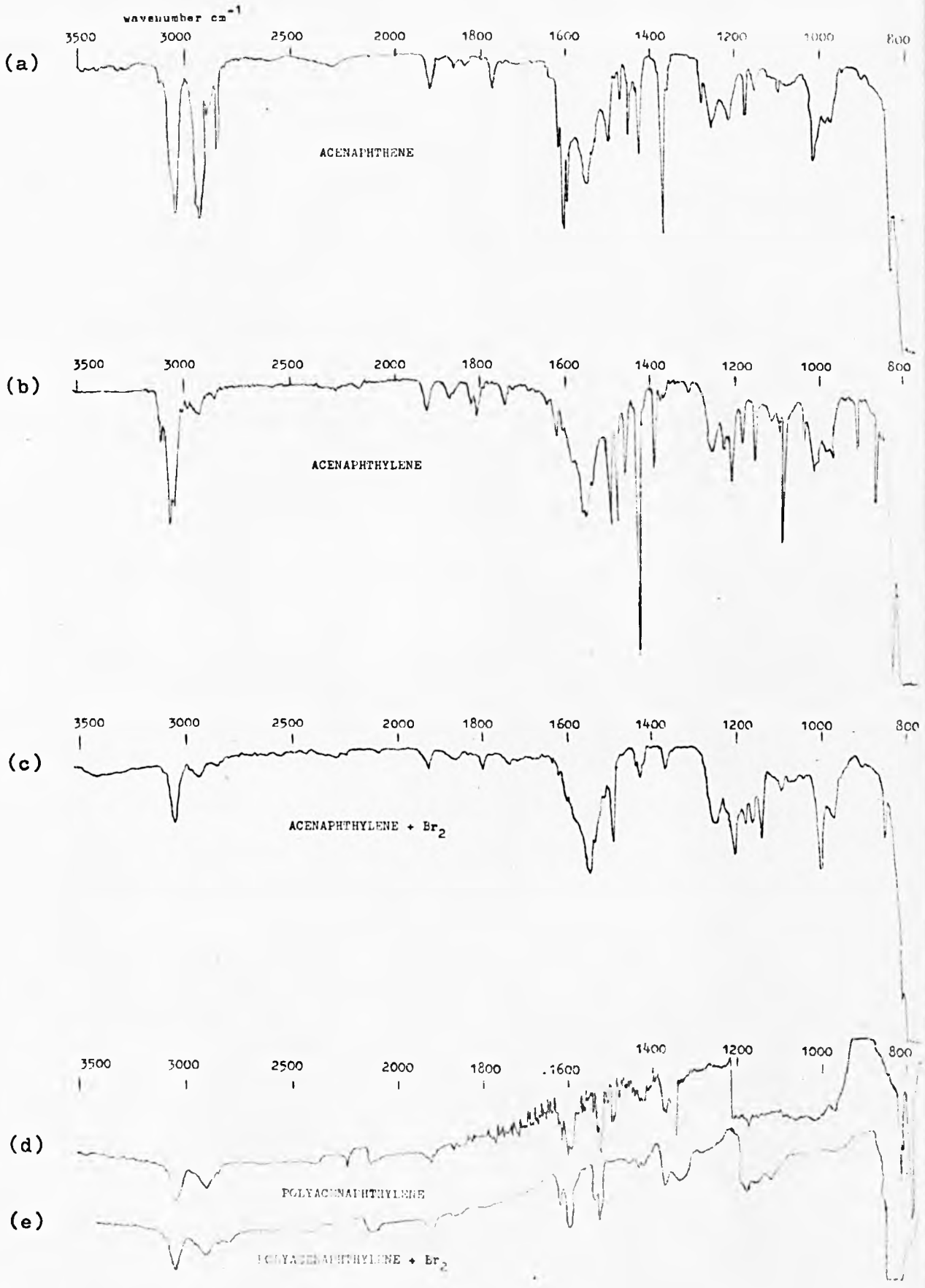
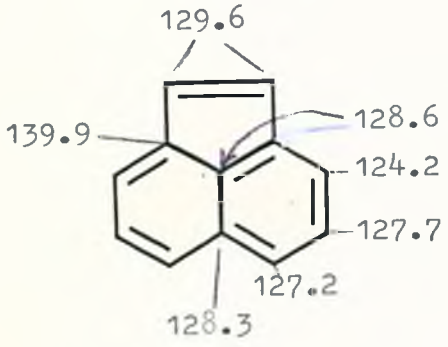


FIGURE 9.9.

^{13}C N.M.R. PEAK POSITIONS RECORDED FOR ACENAPHTHYLENE (p.p.m.)



types of carbon atom present. Figure 9.9. displays the frequencies which were recorded and assigns them to the various carbon atoms; the values obtained agree closely with published data[22].

Trace (b) in Figure 9.8. is a COM spectrum of polyacenaphthylene, the broad peak at lower field is due to the -CH-CH- absorptions along the polymer backbone. The narrow peaks in the monomer spectrum now appear broad: this is characteristic of polymers. It is interesting that the absorption from the quaternary carbon atom at 139.9δ has remained, and this suggests that there is some (1,8 C=C) unsaturation in the polymer. To test this hypothesis concentrated sulphuric acid was added to the deuterated chloroform solution of polyacenaphthylene to observe the "protonated" polymer. Trace (c) is the COM spectrum of the resultant mixture. The most notable features are (i) the removal of the narrow splitting (trace (b)), (ii) the resolution of the broad multiplet into a broad doublet of doublets. A reduction in the area of the quaternary carbon atom absorption (at 139.9δ) compared with trace (b) has occurred, whilst the area of the absorption at 145δ stayed approximately constant. This implies that either there are some (1,8 C=C) groups still present, or that the peak at 139.9δ is characteristic of the "protonated" polymer. The investigation for terminal unsaturation by the ^{13}C N.M.R. method was discontinued at this stage in favour of U.V. analysis because it was postulated that addition of the sulphuric acid, or indeed, any reagent, to the polyacenaphthylene might result in unknown side reactions with the aromatic system , and could possibly give rise to spurious peaks in a ^{13}C N.M.R. spectrum.

Figure 9.10. shows the U.V. spectra which were obtained for

FIGURE 9.8. SPECTRA OBTAINED DURING ^{13}C ANALYSIS(δ)

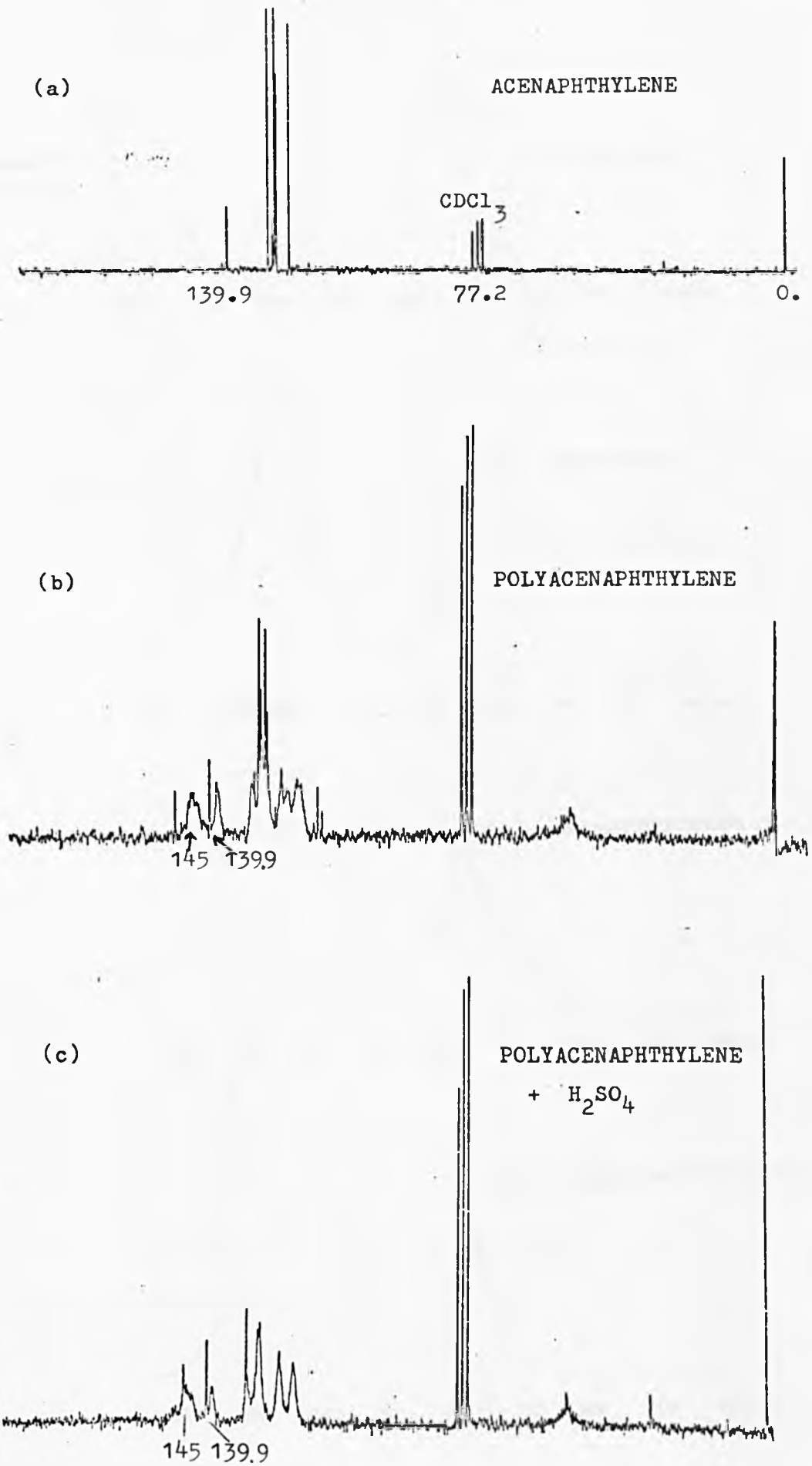


FIGURE 9.10. SPECTRA OBTAINED DURING U.V. ANALYSIS

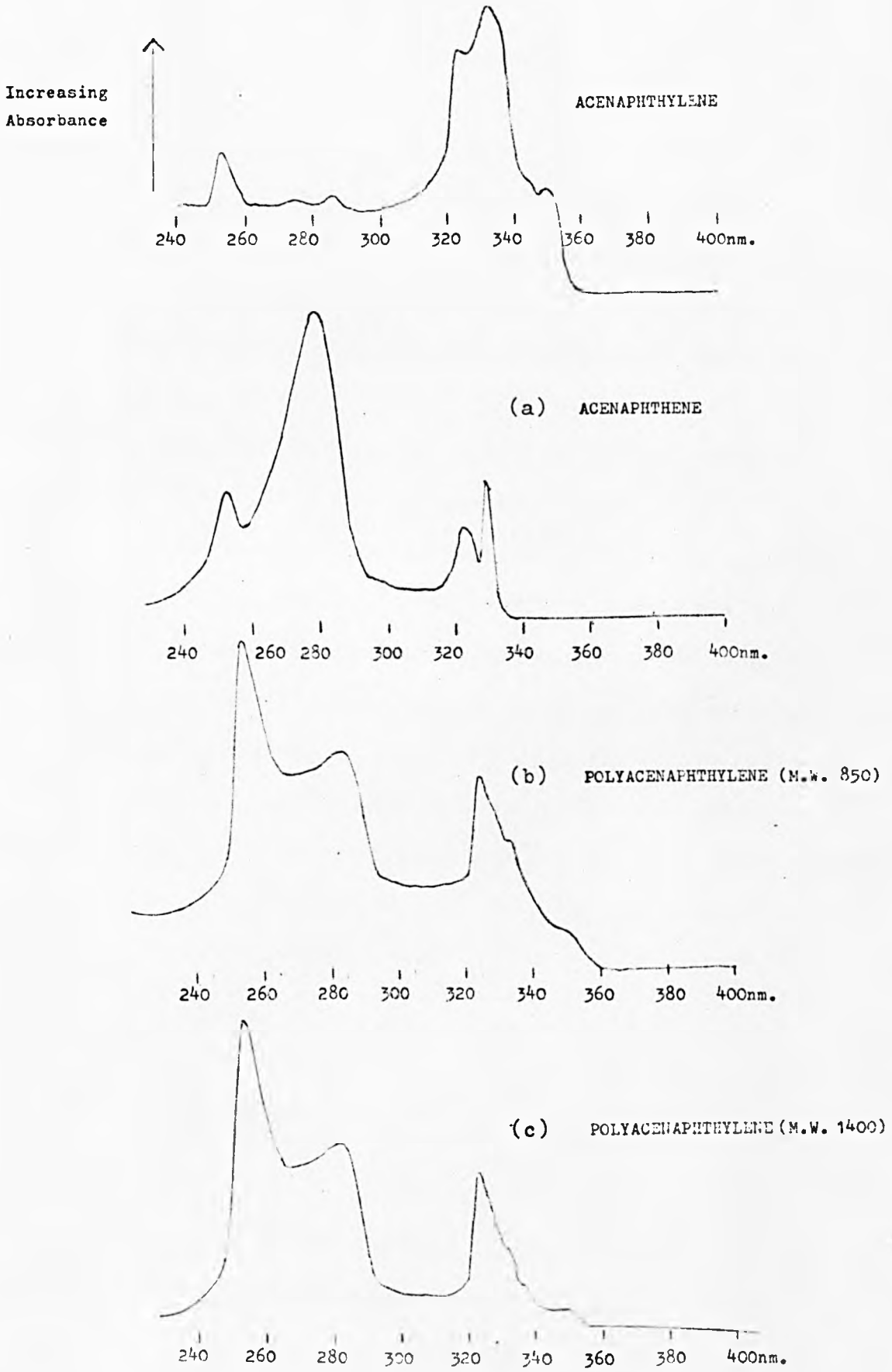
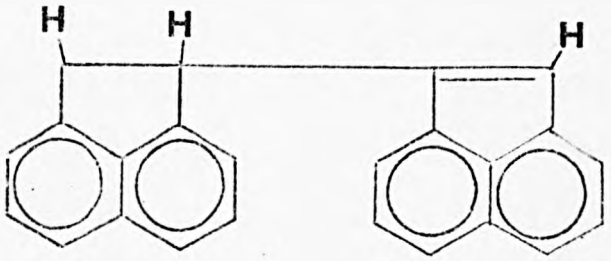


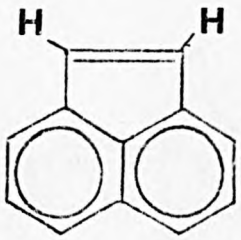
FIGURE 9.10.1.

COMPARISON OF THE C=C IN POLYACENAPHTHYLENE, ACENAPHTHYLENE, STYRENE AND α-METHYLSTYRENE

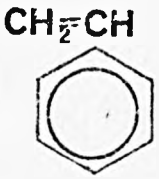
(a)



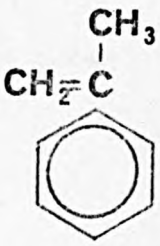
(b)



(c)



(d)



acenaphthylene, acenaphthene and polyacenaphthylenes of 850 and 1400 M.W.

A correlation can be made between most of the peaks present in all four spectra. On comparison of the acenaphthylene and acenaphthene spectra an absorption at 350nm (which may be attributed to the (1,8 C=C unit) is the only difference observed. This absorption is also present in both polyacenaphthylene spectra, and is of higher intensity in the lower polymer. Therefore, it can be suggested that the absorption at 350nm is definitely due to the (1,8 C=C).

From the following analysis the number of polymer chains which possess the (1,8 C=C) unit can be determined.

The assumption made in this calculation is that the ε_{350} of the (1,8 C=C) in the polymer and of a monomer molecule are the same. This assumption is not unreasonable on the basis of the following facts: in the monomer (a) there are two hydrogen atoms attached to the (1,8 C=C) bond, whereas in the polymer (b) one of the hydrogen atoms is replaced by a carbon atom (Figure 9.10.1.). An analogous system is styrene (c) and α-methylstyrene (d), in which the β-hydrogen atom is replaced by a carbon atom; the alteration in ε is from 1.48×10^{5} (styrene) to 1.08×10^{5} moles^{-1}l cm (α-methylstyrene)[23].

Let $n = [C{=}C_{1,8}] \propto A$, where A = absorbance at 350nm

$[\bar{P}_n]$ = [Polymer] for(SK132) 3.08×10^{-6}M, for(SK141) 3.58×10^{-6}M

$m = 1.46\times10^{-5}$M

from $A_m = \varepsilon\, m.l.$ (where the path length l = 1.0cm)

For the monomer, the absorbance (A_m) was 62*

therefore $\varepsilon = \frac{62}{1.46\times10^{-5}} = 4.25\times10^{6}$ mole^{-1}cm l

* Obtained with a mask over U.V. light beam.

Likewise, $A'_p = \varepsilon n_1 l$ and $A''_p = \varepsilon n_2 l$

where A'_p is absorbance at 350nm for polymer solution (SK132)

and A''_p is absorbance at 350nm for polymer solution (SK141)

$$n_1 = A'_p / \varepsilon l = 10/4.25 \times 10^6 = \underline{2.35 \times 10^{-6} M}$$

$$n_2 = A''_p / \varepsilon l = 18.6/4.25 \times 10^6 = \underline{4.4 \times 10^{-6} M}$$

$$\text{Thus, } n_1 / [\bar{P}_n]_{(SK132)} = 2.35 \times 10^{-6}/3.08 \times 10^{-6} = \underline{\underline{0.77}}$$

$$n_2 / [\bar{P}_n]_{(SK141)} = 4.4 \times 10^{-6}/3.85 \times 10^{-6} = \underline{\underline{1.1}}$$

Therefore, for the higher polyacenaphthylene approximately 80% of the chains have terminal unsaturation and for the lower polymer there is on average one (1,8 C=C) unit per chain. From comparison of the ε values reported for styrene and α-methylstyrene the assumption that the ε for the (1,8 C=C) unit in the polymer and monomer are the same appears valid. The other sources of error in the unsaturation measurements are those associated with (i) weighing of the materials, (ii) adding the required volume of THF and (iii) measurement of peak heights. A conventional assessment of the uncertainty in the values 0.77 and 1.1 was obtained (by method given in Appendix) in terms of the measurements performed and gave a limit of ±5%.

9.2. Discussion of Results

9.2.1. Kinetics

If the rate-determining step in the polymerisation is a bimolecular reaction between a growing cation and monomer, as shown in equation (9.4.)

$$[P_n^+] + M \xrightarrow{k_p} [P_{n+1}^+] \qquad (9.4.)$$

$$\text{then} \quad -dm/dt = k_p [P_n^+] m \qquad (9.5.)$$

where $[P_n^+]$ is the concentration of the growing carbenium ions

k_p is the rate constant of propagation

and M is a monomer molecule

Experiments carried out in this study have shown that $-dm/dt = k_1 m$ and that $k_1 = k_2 c$ (Figures 9.1. and 9.2.). If initiation is fast and complete then $[P_n^+] = c_o$ and $k_2 = k_p$, where k_2 is a second order rate constant and so $k_1 = k_p [P_n^+]$: therefore a plot of k_1 vs. c_o should give a line with slope = k_p.

The slope of the graphs k_1 vs. c_o in Figure (9.2.) for the experiments in which the apparatus was pumped for 8 hours before initiation by the propionyl or nitronium salt are found to be the same (within experimental uncertainty): 1.66 $mole^{-1}$ l s^{-1} (propionyl) and 1.73 $mole^{-1}$ l s^{-1} (nitronium). The average of the slopes and the slope of the best line through all the points, are identical:

1.69 ±0.04 mole^{-1} l s^{-1}. Thus, the slope of the plot of k_1 vs. c_o is independent of the type of catalyst used.

From the U.V. analysis to determine the active-end concentration $[P_n^+]$, a slight discrepancy between the c_o and $[P_n^+]$ values was found. Possible reasons for the discrepancy are given in section 9.2.2. It is concluded that k_2 can be identified as k_p for both the propionyl and the nitronium systems.

Since the polymerisations were carried out in a solvent system of high dielectric constant (> 30) and the concentration of growing ends was low (10^{-4}M), the concentration of ion-pairs will be so low that the k_p measured can be identified with k_p^+, the rate-constant due to free ions.

A check on the k_p is made in the following calculation:

$$-dm/dt = k_p\ m\ c_o$$

and $$k_1 = k_p\ c_o$$

therefore $$k_p = k_1/c_o$$

If a random value of c_o is used (Figure 9.1.)

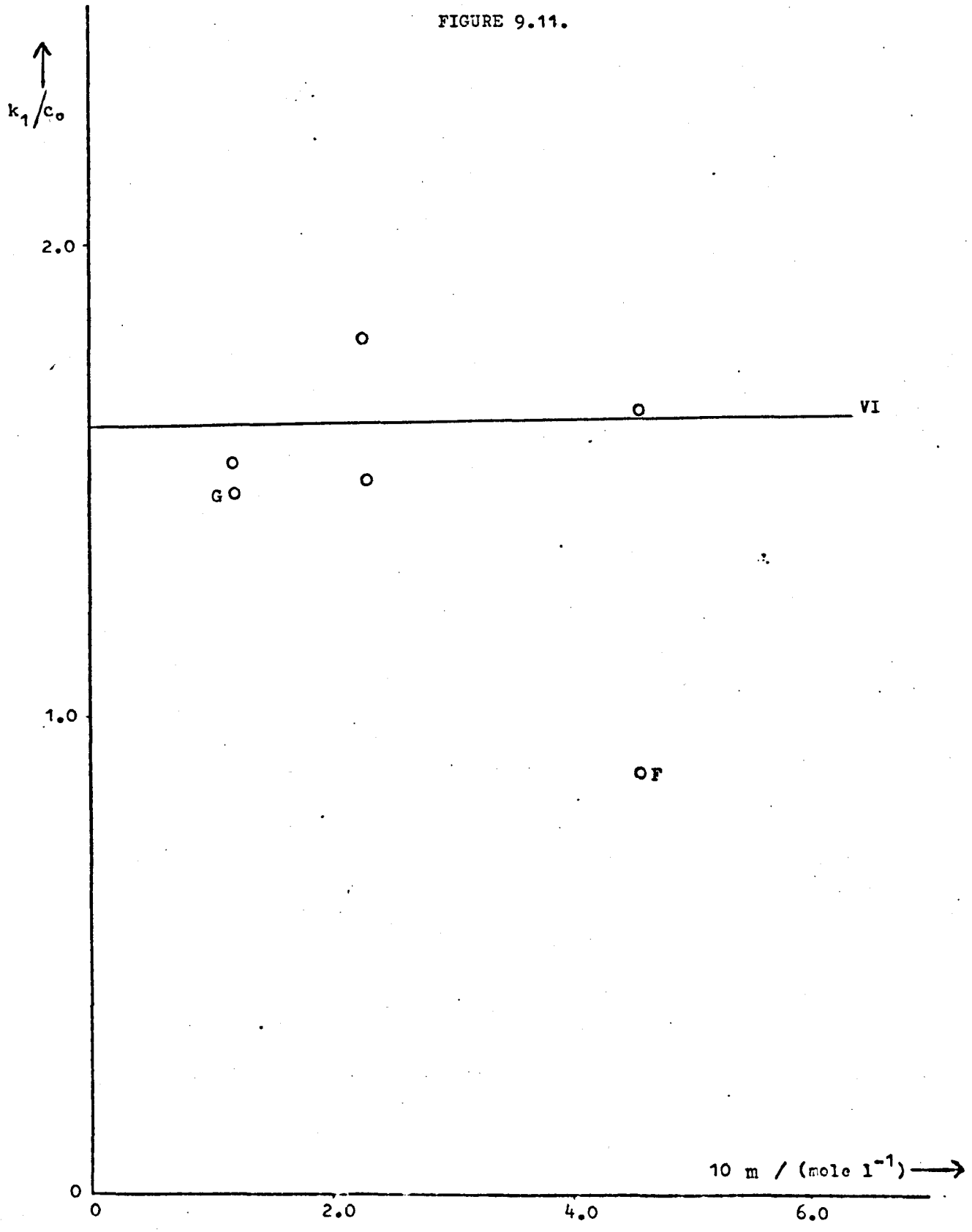
$$k_p = 10^{-3}/5\text{x}10^{-4}$$

$$\underline{k_p = 2 \text{ mole}^{-1} \text{ l s}^{-1}}$$

This value is in good agreement with the k_p obtained from the plot of k_1 vs. c_o Figure 9.2. . Figure 9.11. shows that the k_1/c_o vs. m plot is a horizontal straight line, which indicates that k_2 is independent of the initial m and therefore k_1 does not alter during the polymerisation. The half-life ($t_{\frac{1}{2}}$) of the polymerisation can

Figure 9.11. shows a plot of k_1/c_o vs. m for the nitronium hexafluoroantimonate initiator over a range of c 10^{-3}-10^{-4}M.

FIGURE 9.11.



also be calculated:

$$t_{\frac{1}{2}} = \ln 2/k_1 = (2.303 \times 0.3010)/10^{-3} = \underline{800s}$$

The $t_{\frac{1}{2}}$ can be compared with the value obtained from the plot of m vs. time (Figure 9.12.). The m at different times can be obtained from equation (9.6.). The derivation of equation (9.6.) is given below:

$$\text{Since} \quad -dm/dt = k_1 m$$

$$-dm/m = k_1 \, dt$$

$$\text{On integration this gives} \quad \ln m = k_1 t + C \qquad (9.6.)$$

C is the constant of integration (=1.47)

Table 9.6. records the calculated m values at the various times. The $t_{\frac{1}{2}}$ obtained from the graph (Figure 9.12.) was 690s which is very close to the calculated value of 800s.

It can be seen from the conversion curve (Figure 9.12.) that after 1.0 hour approximately 97% of the monomer has been consumed and there are four half-lives during a 50 minute period; (i) 690s (ii) 1350s (iii) 2010s and (iv) 2820s. This is consistent with the observations recorded during the polymerisations, (1) that after a 50 minute period the dilatometer readings remained constant (section 8.2.2.) and (2) that from the plot of log $[(h_o - h_\infty)/(h_t - h_\infty)]$ vs. time (equation (9.1.)) four half-lives were usually recorded.

Figure 9.12. shows the conversion plot of m vs. t for SK128 where the m=0.23M and c_o= 1.05 x 10^{-3}M (propionyl hexafluoroantimonate)

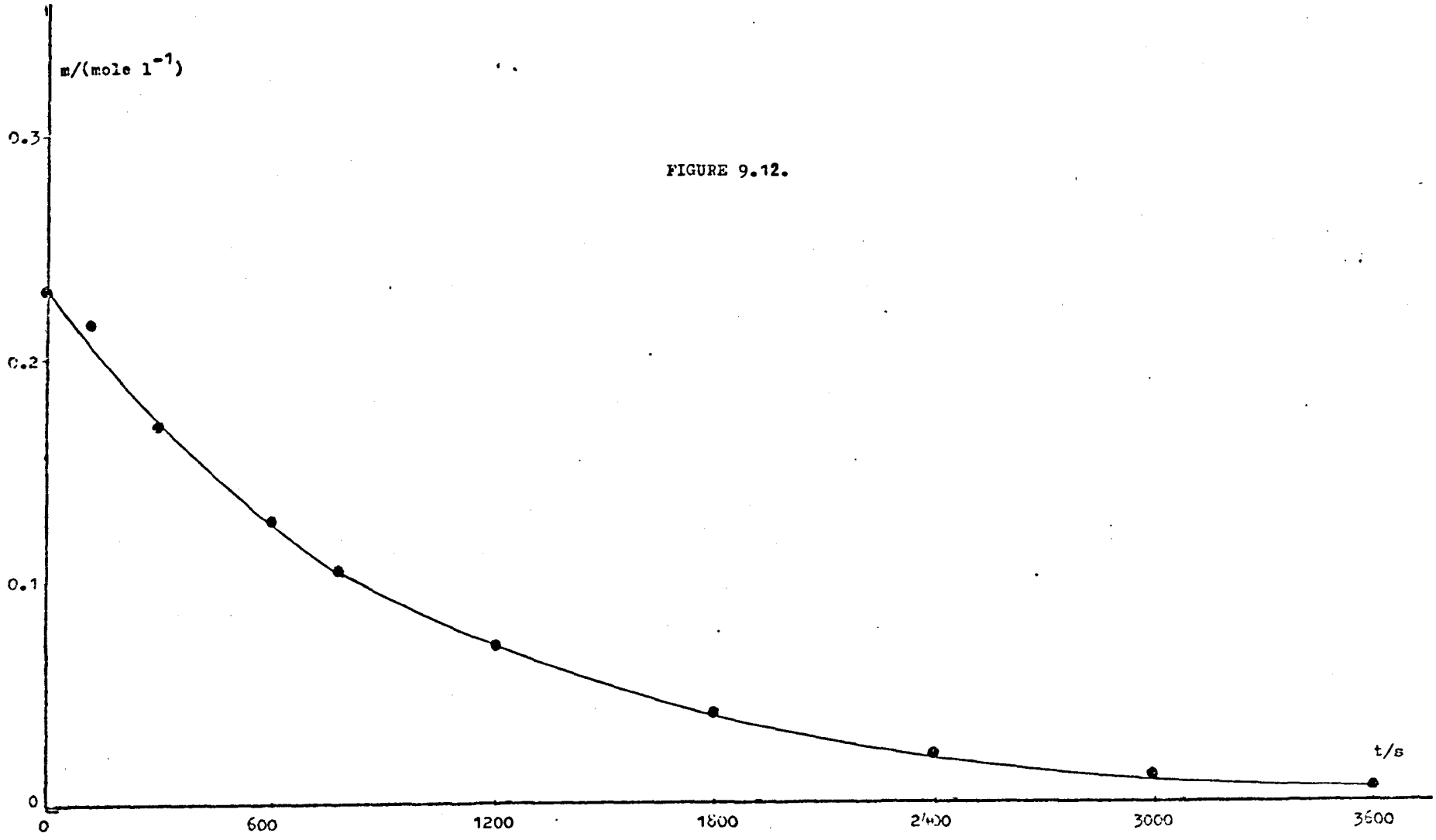


FIGURE 9.12.

TABLE 9.6

DATA FOR THE CONVERSION CURVE (SK128).

m/(mole ℓ^{-1})	t/s
0.230	0
0.216	60
0.170	300
0.126	600
0.105	780
0.070	1200
0.040	1800
0.020	2400
0.011	3000
0.006	3600

(9.7.) $$\frac{1}{DP_n} = \frac{k_m}{k_p^+} + \frac{1}{k_p^+ m}\,(k_t + k_c c_o \quad\quad + k_s\,[S] + J)$$

Where k_m/k_p^+ is the chain breaking coefficient due to monomer

k_p^+ is the rate constant of propagation for free ions

k_t is the rate constant of unimolecular termination

k_m is the rate constant of chain breaking reactions by monomer

k_a is the rate constant of chain breaking reactions by co-catalyst

k_s is the rate constant of chain breaking reactions by solvent

c_o is the concentration of catalyst

$[S]$ is the concentration of solvent

J is a term which includes as yet unidentified chain breaking reactions

(9.8.) $$\frac{1}{DP_n} = \frac{k_c}{k_p^+}\,c_o + \frac{1}{k_p^+}\,(k_t + k_m\,m \quad\quad + k_s[S] + J)$$

Where k_c/k_p^+ is the chain breaking coefficient due to catalyst.

Since k_p has been identified as k_p^+, the k_t term (rate constant of unimolecular termination) is irrelevant.

* For a full algebraic derivation and detailed discussion of the Mayo plots, Plesch's review[24] on "Cationic Polymerisation" should be consulted.

9.2.2. DP

Pác and Plesch[25] have shown that the Mayo plots are applicable to polymer at high as well as low conversion. The Mayo plots were used to rationalise the kinetic data which was obtained in the present study.

The molecular weights of the polymers were much lower than those calculated from c_o on the assumptions (a) that the number of active ends is equal to the c_o, and (b) that there are no chain-breaking reactions (Table 9.4.). To consider the latter criterion: Figure 9.13. shows the first Mayo plot[24] (1/DP vs. 1/m) for the results which were obtained with the nitronium initiator. The intercept of this graph, k_m/k_p^+ is a measure of the relative rate of chain transfer due to monomer (equation (9.7.)). The graph shows clearly the unreliability of points F and G, but the remaining points all lie on the straight line VII which has an intercept of 0.13.

Line VIII (shown in Figure 9.14.) is the second Mayo plot (1/DP vs c_o) for the results derived from polymerisations which were initiated by the propionyl salt. The slope of this graph, k_c/k_p^+, is a measure of the relative rate of chain transfer due to initiator, and the intercept is a measure of all other transfer reactions (equation (9.8.)).

There is no definite evidence that any reagent derived from the catalyst is involved in chain breaking reactions.

The second Mayo plot (Figure 9.14.) has shown that chain transfer with catalyst is negligible. As with cationic vinyl polymerisations, one of the most important chain transfer reactions in the present system involves the monomer: it is a ß-proton transfer from the growing end to a monomer molecule (equation (9.9.));

Figure 9.13. shows the first Mayo plot of 1/DP vs. 1/m for the nitronium hexafluoroantimonate initiator (10^{-3}-10^{-4}M) at variable m (0.115-0.46M). Points F and G are seen to be inconsistent with the other data obtained.

FIGURE 9.13

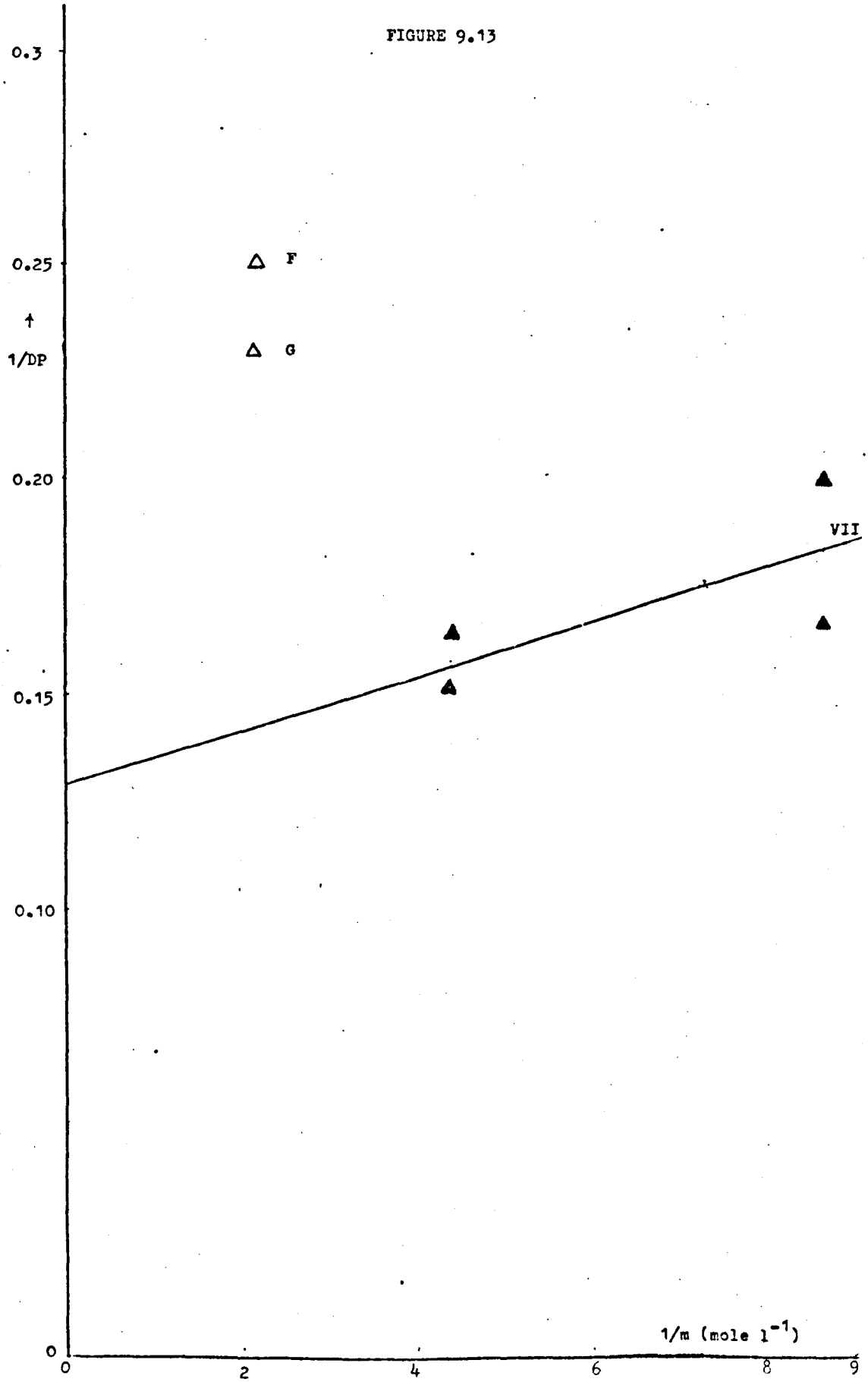
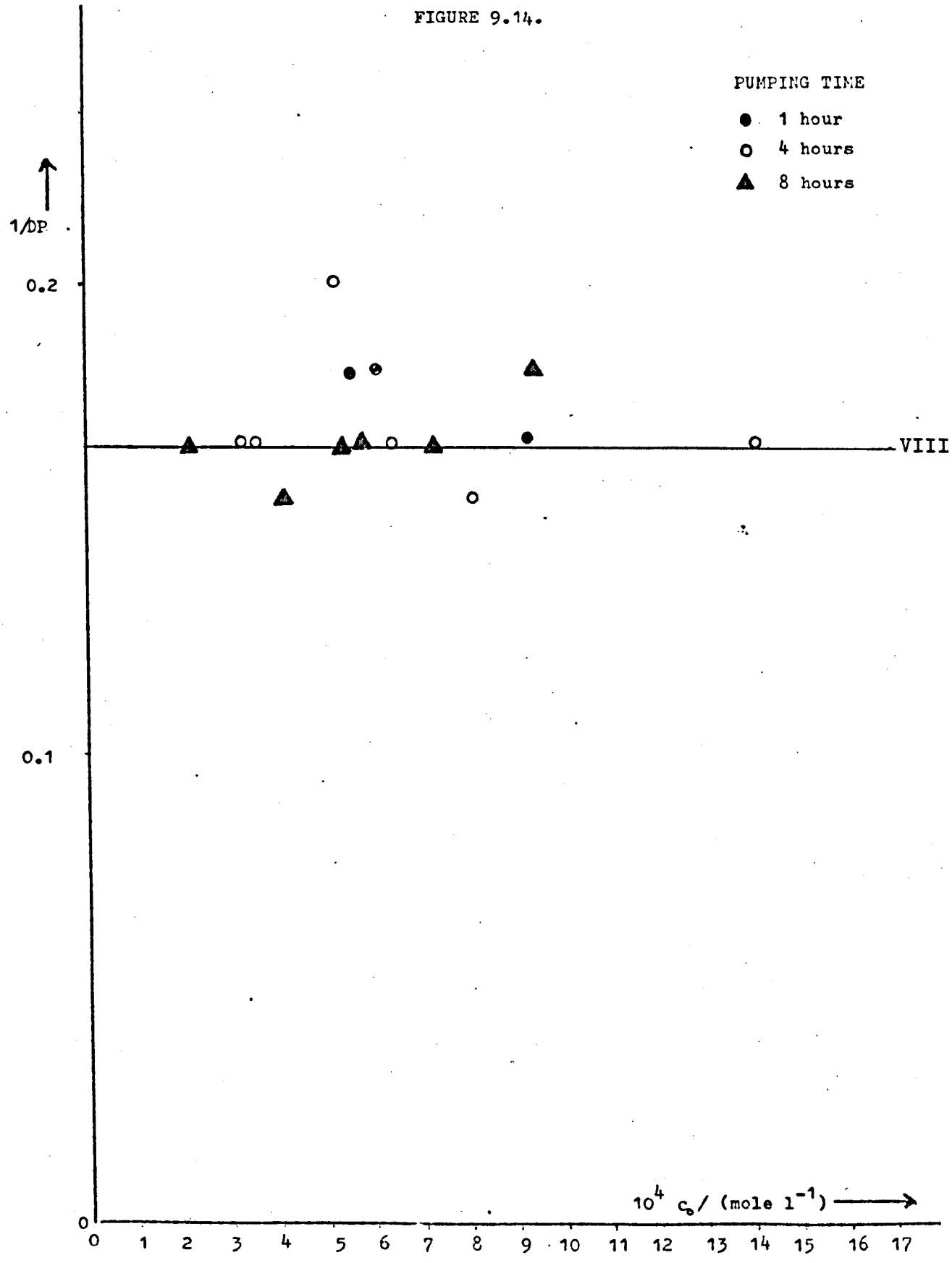
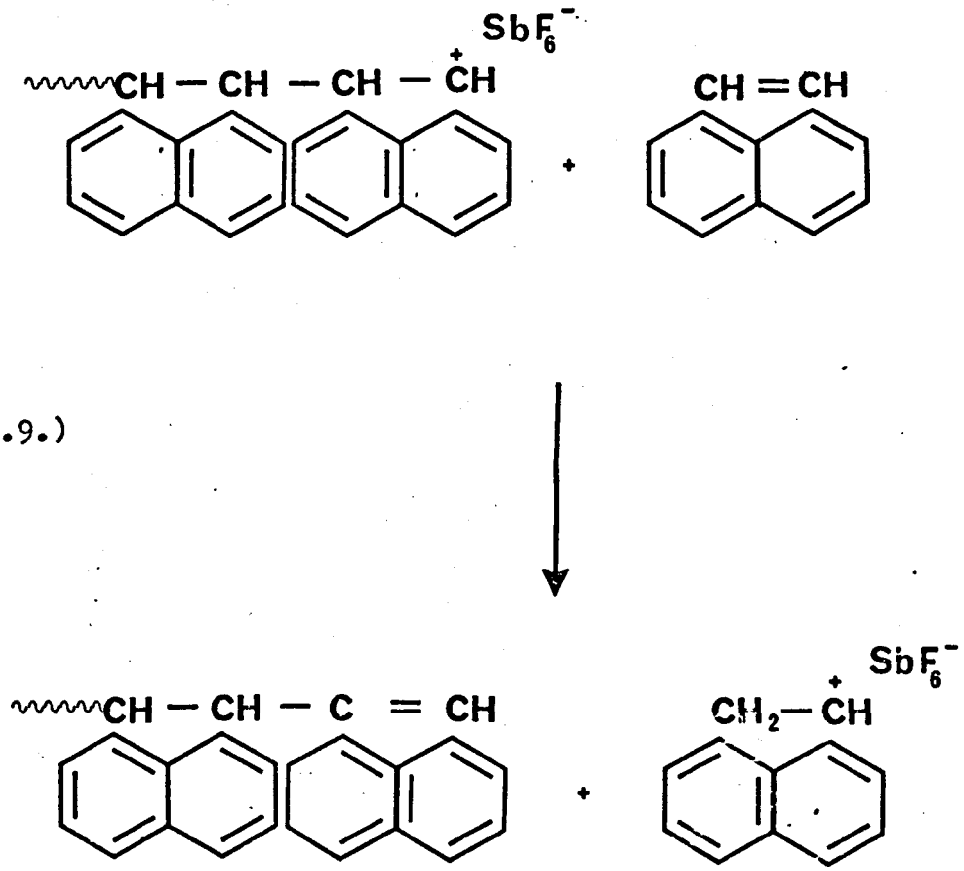


Figure 9.14. shows the second Mayo plot of 1/DP vs. c_o for the propionyl hexafluoroantimonate initiator (10^{-3}-10^{-4}M) at a constant m (0.23M).

FIGURE 9.14.


PUMPING TIME
1 hour
4 hours
8 hours
1/DP
0.2
0.1
0
VIII
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17
10^4 c_o / (mole l^{-1})



(9.9.)

evidence for this is shown by the (1,8 C=C)analysis and first Mayo plot (Figure 9.13.)) which gives k_m/k_p^+ equal to 0.13. A value for k_m can be obtained from equation (9.7.) by means of the k_p^+ obtained in the previous section.

$$k_m/k_p^+ = 0.13$$

$$\underline{k_m = 0.22 \text{ mole}^{-1} \text{ l s}^{-1}}$$

From equation (9.8.), the intercept of the second Mayo plot is equal to k_{tr}/k_p^+, where k_{tr} is overall rate constant for all transfer reactions except that with catalyst.

$$k_{tr}/k_p^+ = (J + k_m\, m)/k_p^+ = 0.16$$

$$J + k_m\, m = 0.16 \times 1.69 = 0.27$$

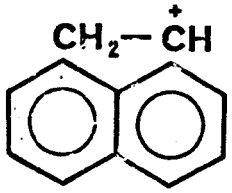
$$J = 0.27 - 0.22 \times 0.23$$

$$= 0.27 - 0.0506 = 0.2194$$

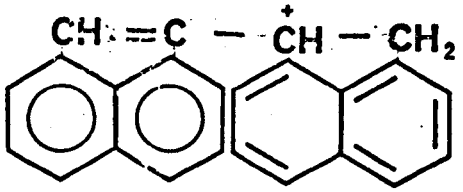
$$= \underline{0.22}$$

Therefore, comparison of k_m with k_{tr} reveals that transfer to monomer is the only chain breaking reaction in this system.

The main impurity in both systems is probably water. Because the concentration of impurities is nearly identical for both initiators, and since variations in the monomer concentration were carried out with the nitronium salt, (which would have altered the concentration of any impurities contained in the monomer) it can be concluded that the solvent or the surface of the dilatometer assembly (Figure 8.4.) and not the monomer were the main source of the impurities.



A



B

9.2.3. U.V. work

A straight line (Figure 9.4.) was obtained for the plot of the $[P_nAN^+]$ and $[P_nCH_2CPh_2^+]$ values against c_o. In theory, this plot should be a straight line which passes through the origin and has a slope = 1 (tan 45^o). The angle of the line in Figure 9.4. is $37^o17'$, which means that the concentration of active ends was $0.83c_o$. This figure is an average value for all the polymerisations which were initiated by the propionyl and nitronium catalysts.

Results of the analyses of polymerised solutions revealed that $[P_n^+]$ was 20-25% lower than c_o. The discrepancy is not thought to be significant because the spectra were recorded in nitrobenzene after the polymerisation had ceased, i.e. when the meniscus in the dilatometer capillary had become stationary, whereas the catalyst concentration was measured in dichloromethane. Therefore, it is possible that the small discrepancy between $[P_n^+]$ and c_o is due to solvents of different dielectric constants being used.

Two features of the U.V. spectra of the polymerisation mixtures are difficult to explain: (i) the presence of peaks at 575nm and 675nm in the U.V. spectrum when the nitronium salt was the initiator used, (ii) the growth of the peak at 575nm at the expense of the peak at 675nm.

As outlined in section 8.2.2., a distinct green colour was obtained when the nitronium catalyst phial was broken, but no such colour was found with the propionyl salt. The U.V. spectra of the polymerisations for which the nitronium salt was the initiator showed peaks at 465, 575 and 675nm as soon as the phial was broken. The growth of the peak at 575nm could correspond to the formation of (1,8 C=C) units in the polymer, but this argument can be dismissed because (1,8 C=C) moieties were found in the polymers which were

initiated by propionyl salt and no peak at 575 or 675nm was observed in their spectra.

On the basis of the information from the four polymerisations which were initiated by the nitronium salt, in which no residual monomer was found, no satisfactory assignment of the peaks 575 and 675nm can be given (see Suggestions For Further Work).

The U.V. absorptions at 445nm for the propionyl and at 465nm for the nitronium systems might be assigned tentatively to the acenaphthylenium ion in nitrobenzene. The wavelength difference between these absorptions and those recorded by Young[21] (he assigned the peaks at 560 and 635nm in H_2SO_4 to be due to the ions A and B respectively shown opposite) could result from the difference in dielectric constant of the solvent. That is, for polymerisations with (1) the propionyl initiator and (2) the nitronium initiator, the solvent systems used were: nitrobenzene plus approximately 5% dichloromethane for (1), and nitrobenzene plus approximately 5% nitromethane for (2). The resulting difference in the dielectric constant of the solvents could alter the position in the U.V. spectrum of the acenaphthenium ion absorption.

A transfer process, which is probably a β-proton transfer from the growing end, occurs in the system. However, this is not totally unexpected because the propagation stage of the acenaphthylene polymerisation is known to be slow[3] and by employing nitrobenzene as the solvent the polymerisation is slowed down even more. Therefore, it is possible that in solvents of lower dielectric constant than nitrobenzene e.g. dichloromethane, side reactions such as the β-proton transfer process occur only very slowly but that in the present system they become more important. Thus, the peaks at 575 and 675nm in the U.V. spectrum of the P_nAN^+ could be due to species which are only formed when a solvent of high dielectric constant is used.

Evidence for the (1,8 C=C) moieties which result from proton transfer was shown conclusively by U.V. analysis as a peak at 350nm. The I.R. and ^{13}C n.m.r. techniques suggested the presence of (1,8 C=C) unsaturation but the U.V. method allowed for the positive identification and for some measure of the unsaturation present to be estimated from the height of the peak at 350nm.

$$(\varepsilon_1 V_1 + \varepsilon_2 V_2) / V_{total} = \varepsilon_{total}$$

Where ε_1 = dielectric constant of nitrobenzene (34.82)

ε_2 = dielectric constant of nitromethane (35.87/ dichloromethane (8.93)

ε_{total} = overall dielectric constant of the solvent system

(9.10.)

V_1 = the volume of nitrobenzene (17-19ml)

V_2 = the volume of nitromethane/dichloromethane (1-3ml)

V_{total} = total volume (20ml)

9.3. Conclusions

The same k_p values were recorded for the two different cationic initiators which possessed the SbF_6^- anion, in solvent systems of high dielectric constant, 33.5 for propionyl salt and 34.8 for nitronium salt*. No evidence to suggest the k_p is dependent on m was found (Figure 9.11.). Therefore k_p is equal to k_p^+.

The k_m value obtained from the first Mayo plot (Figure 9.13.) was in very close agreement with the calculated k_{tr} value.

The absorption of the acenaphthenium ion was found to be present at 445nm for the propionyl system and at 465nm for the nitronium system. The difference in the position of the acenaphthenium ion absorption is unlikely to be due to the initiating species but to some solvent effect. However, there appears to be an unresolved discrepancy because Young assigned the absorption in sulphuric acid to be at 560nm.

The peaks recorded at 575 and 675nm in the U.V. spectrum of the polymerisation mixture which was initiated by the nitronium salt were not assigned. (see Suggestions For Further Work).

* These values are calculated from equation 9.10.

9.4. Suggestions For Further Work

(1) A U.V. study with the nitronium hexafluoroantimonate initiator should be carried out in an attempt to assign the peaks at 575nm and 675nm. To prove conclusively that the λ_{max} of the acenaphthenium ion in nitrobenzene has shifted from 560nm to the 450nm region, the absorption of the triphenyl carbenium ion in nitrobenzene and in sulphuric acid should be recorded and the λ_{max} in each solvent compared. This investigation could be incorporated as part of a continued study of the polymerisation of acenaphthylene by this initiator, since only six experiments, two of which are suspect, were performed with it.

(2) Since only the propionyl system was investigated to any reasonable extent (the nitronium salt providing a comparison) more work should be undertaken with different initiators in nitrobenzene with acenaphthylene to complement the present work.

(3) Several permutations of c_o and m may be tried in nitrobenzene, and then in a solvent such as dichloromethane, to compare the kinetics in each solvent. This investigation could be designed to encompass a very wide concentration range because the present study was limited to the range 10^{-3} - 10^{-4}M for c_o and 10^{-1} for m.

(4) The investigation could be extended to include other monomers but retaining the salt initiators and nitrobenzene.

Uncertainty Assessment

For any measurement which was recorded the error present in the height, weight, area etc. was estimated by the method shown in the example below:

$$\text{From } X = n/[P_n] \qquad \text{(section 9.1.4.)}$$

where X is the number of (1,8 C=C) units per polymer chain

The error in obtaining a value for X can be rationalised as follows;

$$dX/X = dn/n + d[P_n]/[P_n]$$

Therefore to consider each parameter, it can be seen from the Beer-Lambert Law that

$$n = A/\varepsilon l$$

$$\text{so } dn/n = dA/A + d\varepsilon/\varepsilon .$$

The error in a single measurement of the peak height is ±5%.

$$P_n = \text{Weight of polymer } (W_p)/\text{Volume of solvent}$$

$$d[P_n]/[P_n] = dWp/Wp + dV/V.$$

The error in the weighings and volume measurements is ±1%.

Therefore, the overall error in the estimation of $[(1,8\ C{=}C)]$ units per polymer chain is ±5.1%.

References to CHAPTER 9.

20. W.J. Moore, "Physical Chemistry", 5th ed. Longman, LONDON, 1972.

21. R.N. Young, J. Chem. Soc. (B), 1969, 896.

22. J.B. Stothers, "Carbon-13 NMR Spectroscopy" Academic Press, NEW YORK and LONDON, 1972.

23. "U.V. Atlas of Organic Compounds", Butterworths, LONDON, 1966.

24. P.H. Plesch, "Cationic Polymerisation", Pergamon Press, LONDON, 1963.

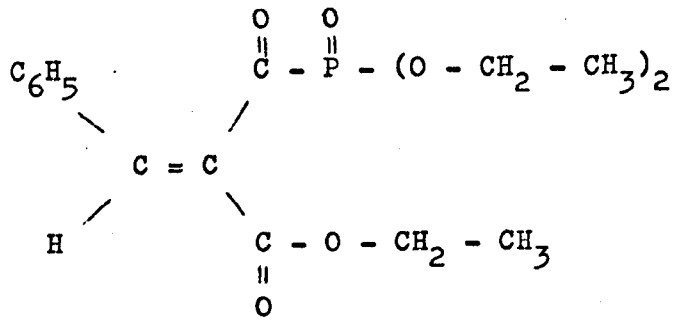
25. J. Pác and P.H. Plesch, Polymer, 1967, 8, 256.

PART D

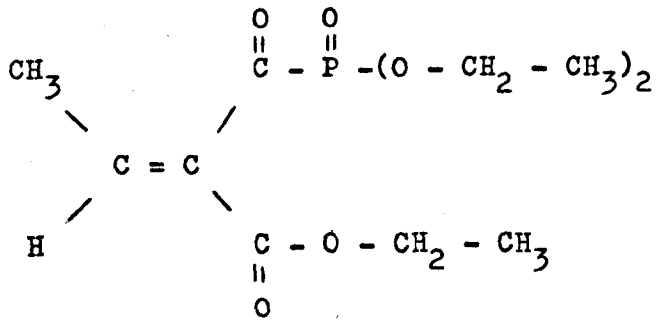
ATTEMPTS TO POLYMERISE PHOSPHORUS-CONTAINING OLEFINS

INTRODUCTION

(1)



(2)



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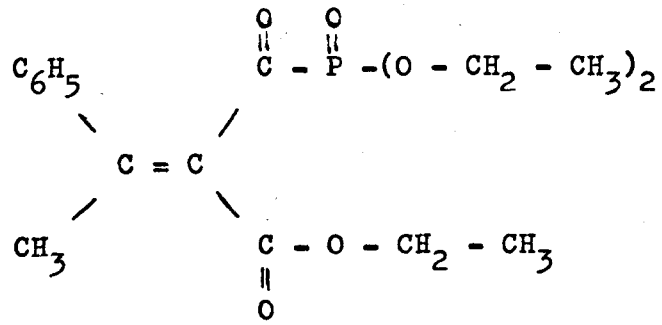

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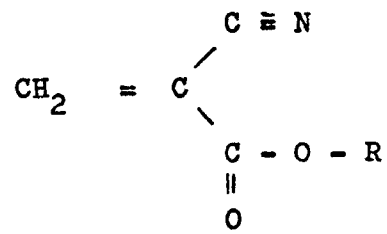


R = alkyl

10.1. Background Chemistry

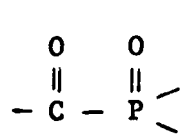
The acylphosphonate and acroylphosphonates, compounds (1) to (3) shown opposite, were prepared by Ph.D. student (Mr. A. Szpala) at the North Staffordshire Polytechnic under the supervision of Dr. J. Tebby. As a result of an approach to Dr. P.H. Plesch for advice on the polymerisability of the compounds a short collaborative project was set up between the two groups of researchers.

The olefins (1 to 3) contain the "phosphocarbonyl unit" $\left[-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{P}}<\right]$ which has an extremely high Hammett σ value[1] as can be seen from Table 10.1. It was postulated that since the strong electron-withdrawing effect of the nitrile group is largely responsible for the rapid polymerisation of the cyanoacrylates (4), under basic conditions[2], polymerisation of the phosphonates should also occur under similar conditions. The σ value of the "phosphocarbonyl unit" is higher than that of the nitrile group, so the charge distribution in compounds (1) to (3) should result in a compound which is more activated towards nucleophilic attack than that derived from (4). Therefore, a series of small scale ionic and free radical polymerisation tests were carried out on the phosphonates to test this hypothesis.

P.m.r. spectroscopy was used to follow the polymerisation since the disappearence of the C=C absorption would have been clearly seen with this technique.

TABLE 10.1

The σ Values of Electron-Withdrawing Substituents

Substituent	σ value	
	0.91	
$-NO_2$	0.78	
$-C\equiv N$	0.66	increasing electron-withdrawing power
$-COOR$	0.45	
$-F$	0.06	

EXPERIMENTAL

10.2.1. Anionic polymerisation

A sample (0.5g, 0.001 mole) of the phosphorus compounds (1→3) were dissolved in purified* THF (3ml), in a p.m.r. tube, the tube flushed with nitrogen and the p.m.r. spectrum was recorded on a 100MHz J.E.O.L. spectrometer.

Addition of a 1.6M n-butyl lithium solution (0.070ml, 0.0001 mole) to the "monomer" solution under nitrogen, was made by syringe at 273K. This was accompanied by a rapid evolution of gas and heat. The p.m.r. spectrum was then recorded. However, the only change in the p.m.r. spectrum from that of the starting material recorded over a two hour period was the total loss of an olefinic proton absorption for compounds (1) and (2), and the loss of a methyl proton absorption for compound (3). The original spectra were obtained on addition of a few drops of methanol at room temperature to the reaction solutions.

A similar experiment with 1.0M THF solution of sodium naphthalene produced no evolution of heat or gas, and after two hours there was no change in the p.m.r. spectrum of the starting material.

10.2.2. Cationic polymerisation

The experimental conditions employed for these tests were similar to those described in the previous section (10.2.1.). That is, the temperature at which initiation was carried out and the concentrations of phosphonate and initiator (BF_3OEt_2, CF_3COOH and $TiCl_4$) were identical to those reported for the anionic polymerisation tests.

The solvent for the cationic work was methylene chloride**. No differences were observed in the physical state of the "monomer" solution after addition of the initiators i.e. no heat was evolved and no changes in p.m.r. spectra were recorded.

* purified as reported in section 2.1.
** purified as reported in section 5.1.

10.2.3. Free radical polymerisation

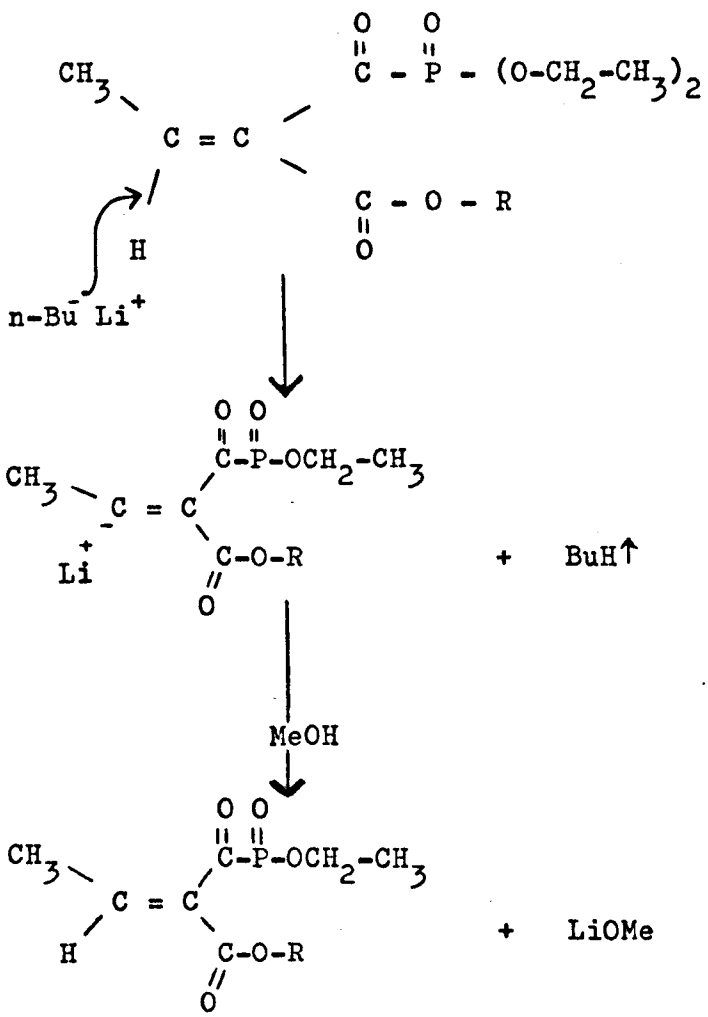
A sample (1g, 0.02 mole) of the phosphorus compound was dissolved in dry benzene (30ml) under nitrogen, before the addition of a 1.0M benzoyl peroxide in benzene solution (1.0ml, 0.001 mole) at 298K was carried out. The mixture was then heated for twelve hours at 333K during which time aliquots (2ml) were removed by syringe, and their p.m.r. spectra recorded.

CONCLUSIONS

10.3. Conclusions

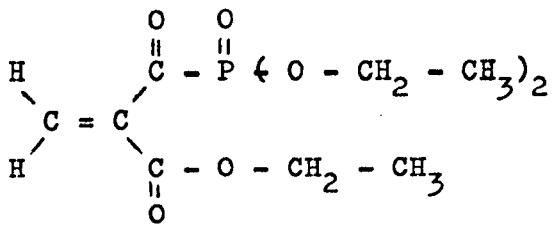
The free radical and cationic polymerisation attempts were unsuccessful since there was no change in the p.m.r. spectra of the original phosphorus compounds before or after addition of the initiators.

Results for the anionic polymerisation attempts can be explained as non-reaction with sodium naphthalene and a metalation reaction when n-butyl lithium is used. The gas evolved was most likely to have been butane as the loss of the proton absorption would correspond to proton abstraction by the butyl anion which resulted in the formation of a carbon-lithium bond and butane gas. This bond is methanolysed readily by methanol to give the starting material and lithium methoxide (equation 10.1).

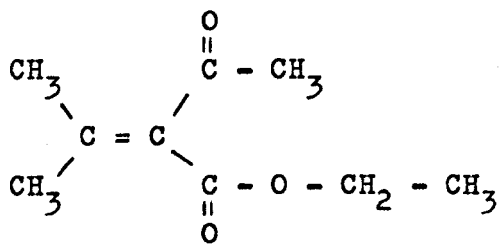


(10.1.)

(5)



(6)



The non-polymerisation of these phosphonates could be assigned to the steric hindrance which exists about the olefinic double bond in compounds (1) to (3). The use of models demonstrates that there is steric interference between the different substituents on the olefinic C=C, which may be reduced sufficiently in the disubstituted analogue (5), for polymerisation to occur. Compound (5) was not tested because it could not be isolated pure.

It must be recognized that the polymerisation tests were exploratory and if an extensive investigation with more stringent conditions were to be undertaken polymerisation of compounds (1) to (3) might be obtained. However, the author is of the opinion that polymerisation is improbable due to steric considerations. Evidence for this view can be gained from examination of the crotonates (6); due to steric hindrance polymerisation cannot occur[3]. Consider the corresponding phosphonate system in which the steric interaction between the ester and the phosphocarbonyl groups is much greater than the steric interaction between the acetyl and ester groups in the crotonates. Therefore, polymerisation of the phosphonates is only likely to occur where the steric interaction is relieved by reducing the size of substituents on the olefinic C=C.

The p.m.r. spectra associated with this work have not been included, at the request of Mr. A. Szpala but are available upon application to his supervisor, Dr. J. Tebby.

References to CHAPTER 10.

1. T. Szpala and J. Tebby, Unpublished Results.

2. "Encyclopedia of Polymer Science and Technology", 1964, 1, 246.

3. " " " " " " 1964, 1, 131.